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# GEOCHIMICA ET COSMOCHIMICA ACTA



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# Geochemistry of arsenic

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ABSTRACT

Chondrites contain an average of about 2 p.p.m. As, distributed as follows: metal phase 12 p.p.m., troilite roughly 10 p.p.m., and silicate phase less than 0·5 p.p.m.

The common igneous rocks do not differ greatly in average arsenic content: granitic rocks 1·5 p.p.m., intermediate rocks 2·4 p.p.m., basalts and diabases 2·0 p.p.m., and gabbros 1·4 p.p.m. Silicic volcanic rocks (3·5 p.p.m.) and serpentines (3–5 p.p.m.) seem to run higher, and ultramafic rocks (1 p.p.m.) a little lower than igneous rocks as a whole. The average for the lithosphere may be taken as 2 p.p.m. As.

Arsenic occurs in quartz, feldspar, and other aluminosilicates, and in iron-ore minerals. The feldspar of igneous rocks probably accounts for one-half or more of the total arsenic. Substitution of arsenic for silicon, aluminium, and iron in the crystal structure is indicated. Arsenic cannot be closely correlated with any major constituent.

The average value for arsenic in shales probably lies in the range 5–15 p.p.m. Shales containing much carbonaceous material or sulphide tend to have more arsenic than others. Sandstones and limestones normally contain less arsenic than shales, and their average is probably not much different from that of igneous rocks. The deep-sea sediments examined average ~10 p.p.m. Because sedimentary material as a whole is richer than igneous rocks in arsenic, significant amounts have escaped from the interior of the earth in the water of thermal springs and as volcanic exhalations. The escaping tendency of arsenic is much smaller than that of H (as $H_2O$), Cl, B, and C, but comparable to that of S.

Arsenic is likely lost in the transformation of slates and graywackes into schists and gneisses in regional metamorphism.

The present paper supplies data on the arsenic content of igneous, sedimentary, and metamorphic rocks, and of meteorites, to supplement the rather scanty available data, especially for the common rocks. An attempt is made to trace the distribution of arsenic and in some measure to account for its behaviour.

## I. PREVIOUS DATA

*Igneous rocks.* Early determinations of arsenic in oceanic sediments, silt, and igneous rocks were reported by CLARKE and STEIGER (1914):

| | *As, p.p.m.* |
|---|---|
| Composite of 51 "red clays" | 6·5 |
| Composite of 52 "terrigenous clays" | trace |
| Composite of 235 samples of Mississippi silt | 3 |
| Composite of 329 American igneous rocks | 4·8 |

The method used is not specified. The average value accepted at present for arsenic in igneous rocks (and the lithosphere) is the one above for the igneous composite.

I. and W. NODDACK (1931) determined the arsenic content of three granites, two basalts, one lava, and two serpentines. The average is 25 p.p.m. As, which doubtless is much too high. They also give arsenic values for many different minerals. The method of analysis is not mentioned.

VERHOOGEN (1948) found 25 p.p.m. As in a tachylite from the Belgian Congo. ÖDMAN (1950) has reported from 100 to 2000 p.p.m. As in Swedish leptites (spectrographic determinations).

*Sedimentary rocks.* Because of the insensitivity of the spectrographic method (limit ~100 p.p.m. $As_2O_5$ or 65 p.p.m. As), GOLDSCHMIDT and PETERS' study (1934) of the geochemistry of

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arsenic was confined largely to sediments rich in iron, manganese, and aluminium, in which arsenic is concentrated by adsorption processes. They found from 100 to 1000 p.p.m. $As_2O_5$ (65 to 650 p.p.m. As) in oxide and hydroxide iron ores of various ages from different regions. (Other data for iron ores, of comparable magnitude, are given in GMELIN (1952, p. 26); also see ÖDMAN, 1950.) Arsenic was also found to be concentrated in sedimentary iron sulphide (as much as 3000 p.p.m. As in zone 3 of the Bell Island, Newfoundland, deposit). On the other hand, arsenic was not detected in metamorphosed iron ores or iron formations, as at the Champion Mine, Marquette Range, Mich., Republic, Mich., and Negaunee, Mich. Sedimentary manganese ores were found to contain less arsenic than iron ores, e.g. 100 p.p.m. $As_2O_5$ (65 p.p.m. As) in the Kutais deposits. Bauxites usually contained detectable arsenic, especially those rich in iron, the maximum being 500 p.p.m. $As_2O_5$ (320 p.p.m. As). Phosphorites contained 100–500 p.p.m. $As_2O_5$. In a number of greensands, from 100 to 500 p.p.m. $As_2O_5$ was found. GOLDSCHMIDT and PETERS also call attention to the large amounts of arsenic in the ash of many coals, usually 500–2000 p.p.m. $As_2O_5$, but sometimes considerably more. Up to 500 p.p.m. $As_2O_5$ was found in the ash of beech humus.

Determinations of arsenic in shales of the Great Plains of the United States have given values from 2 to 42 p.p.m. (WILLIAMS and WHETSTONE, 1940; SLATER *et al.*, 1937). Cretaceous formations of South Dakota contain from 0·2 to 64 p.p.m. As (MOXON *et al.*, 1944). HOEHNE and PETRASCHECK (1936) found from 100 to 1100 p.p.m. $As_2O_5$ (65 to 720 p.p.m. As) in fifteen slates of Silesia and Bohemia, and 100 to 300 p.p.m. $As_2O_5$ in four Carboniferous fireclays and clay-iron stones.

Sandstones and limestones are normally low in arsenic. Two sandstones from Hesse contain 1·5 and 2·3 p.p.m. As (BÜLOW and OTTO, 1931). WYLLIE (1941) obtained an average of 2·4 p.p.m. As in seventeen Ontario limestones.

TREMEARNE and JACOB (1941) found from 0·4 to 18 p.p.m. As in sedimentary phosphate deposits. No definite relation between arsenic and phosphorus was evident; rather, arsenic increased with the iron and carbon content.

In addition to the CLARKE and STEIGER arsenic values for oceanic sediments, we have those of BÜLOW (1935) for the Atlantic Ocean, which average 4 p.p.m. As. FEDOSOV (1940) has reported 3·2–12·7 p.p.m. As for the muds of the Azov Sea.

*Sulphides.* Sedimentary pyrite always contains appreciable amounts of arsenic, ranging perhaps from 10 to 50 p.p.m. As (*Gmelin's Handbuch*, 1952, p. 27; HEGEMANN, 1947–49; TALLURI, 1951) to several tenths of a percent. Pyrite in coal tends to be rich in arsenic and may contain 1000–3000 p.p.m. (GOLDSCHMIDT and PETERS, 1934). Non-sedimentary pyrite often contains much arsenic. Contents of tenths of a percent or even 1–2 per cent As are encountered; with the higher amounts, arsenic minerals are present as inclusions. A pyrite from Leadville, Colo., contains only 140 p.p.m. As (ONISHI).

According to GOLDSCHMIDT and PETERS (1934), magmatic sulphides contain about 2000 p.p.m. As, but according to the NODDACKS only 60 p.p.m. (1931). Pyrrhotite from Norway was found to contain 20–200 p.p.m. As (NODDACK, 1931).

*Meteorites.* I. and W. NODDACK (1931) obtained the following values:

| | As, *p.p.m.* |
|---|---|
| 3 stones | 5–30; avg. 15 |
| 3 irons | 40–300; avg. 160 |
| 3 troilites | 100–600; avg. 300 |

Later they reported 18 p.p.m. As as the average for chondrites (NODDACK, 1934). JOHNSON and NORMAN (1943) obtained some semi-quantitative results spectrographically:

| | As, *p.p.m.* |
|---|---|
| 1 stone and 1 pallasite | 10–100 |
| 1 iron and 3 stones | <100 |
| 2 irons and 10 stones | not detected |

RØER (GOLDSCHMIDT, 1937) found less than 10 p.p.m. As in the Cape York iron.

For comparison it may be noted that terrestrial iron contains relatively much arsenic (Goldschmidt and Peters, 1934): iron in basalt, Bühl, Kassel, 100–500 p.p.m. As; Ovifak iron, 500 p.p.m. or slightly more As; josephinite, Oregon, 2000 p.p.m. As (Clarke, 1924, p. 334).

## II. Analytical Method

The procedure for arsenic in silicate rocks has been described in detail (Onishi and Sandell, 1953). It consists in fusion of the sample with sodium hydroxide-peroxide, evolution of arsine from the filtrate of the leached melt, absorption in iodide-iodine-sodium bicarbonate solution, and final photometric determination of arsenic as heteropoly molybdenum blue with ammonium molybdate-hydrazine sulphate. Samples of 0·5 g were usually taken, and transmission measurements were made with a Leitz-Rouy photometer (640-m$\mu$ filter) in a 1-cm cell. For less than 1 p.p.m. As the error is not likely to exceed $\pm$0·2 p.p.m. For 1 to 2 p.p.m. As the error should be within 20 to 10 per cent, and for larger amounts of arsenic it is proportionately less. The average difference in twenty-five sets of duplicate determinations recorded in the following tables is 4 per cent.

Carbonate rocks (0·5 g or more) were treated with 4 *M* hydrochloric acid at room temperature. If an appreciable amount of residue remained it was filtered off and fused with sodium hydroxide-peroxide. Arsenic was then determined in the combined solutions.

Magnetite and ilmenite were fused with quartz powder (of known arsenic content) and sodium hydroxide-peroxide. The fusion was repeated to recover arsenic remaining in the residue.

Iron meteorites (0·5 g) were dissolved in aqua regia and the solution was evaporated to a paste on the steam bath. Sulphuric acid (1 : 1) was added to the residue and the solution was evaporated to slight fumes. The residue was taken up in concentrated hydrochloric acid, transferred to a Scherrer-type distillation flask, and arsenic trichloride was distilled after addition of hydrobromic acid and hydrazine sulphate (Rodden, 1940). Tests with standard steels showed satisfactory recovery of arsenic.

For determination of total arsenic in chondrites, the sample was first fused with sodium hydroxide-peroxide and arsenic determined in the leach. The residue was treated with aqua regia and arsenic distilled as the chloride after elimination of nitric acid, followed by photometric determination.

In determining arsenic in the component phases of chondrites, magnetic separation was used to give three fractions: metal with some silicate and troilite, troilite with silicate, and silicate with some troilite. The metal phase was treated briefly with 1 *M* hydrochloric acid containing bromine to remove some of the sulphide. This treatment still leaves sulphide with the metal, but it was not considered necessary to apply a correction for this, because the arsenic content of the troilite does not differ much from that of the metal. A correction was applied for silicate in the metal. The mixture of troilite and silicate was treated with cold dilute hydrochloric acid containing bromine. Aliquots of the filtered solution were analyzed for sulphur and arsenic; since the arsenic content of the silicate phase is very low, solution of some of the silicate in acid will not contribute much arsenic,

and the arsenic content of troilite can be found from the As : S ratio. Finally, the silicate fraction containing some sulphide was treated for five minutes with 1 *M* hydrochloric acid containing bromine, and arsenic was determined in the washed residue.

Negligible amounts of arsenic were introduced from the steel mortar in the crushing of rocks and meteorites.

## III. ARSENIC IN ROCKS AND MINERALS

### A. *Igneous rocks*

Both composites and individual samples have been analyzed to obtain average values for arsenic in common rock types and to show the dispersion of arsenic content.

Table 1 gives the arsenic content of composites prepared by mixing equal weights of individual samples. Tables 2–7 give the arsenic contents of individual samples arranged according to rock class. Literature references to some of these

*Table* 1. *Arsenic in composites of igneous rocks**

| *Silica range* % $SiO_2$ | *Average silica* % $SiO_2$ | *Rock type and number of samples* | *Region* | As *p.p.m.* |
|---|---|---|---|---|
| 80·6–76·3 | 77·7 | Granite (12) | U.S.A. | 1·5 |
| 81·5–75·1 | 77·0 | Granite (8) | U.S.A. and Canada | 1·0 |
| 77·4–71·5 | 74·1 | Granite, etc. (9)[1] | California | 1·8 |
| 76·8–68·2 | 73·4 | Granite (7) | Texas (Llano region) | 2·9 |
| 74·3–70·6 | 72·6 | Granite (7) | Canada | 1·0 |
| | | Granite (8)[2] | Canada | 1·0 |
| | | Granitic (5) | Minnesota | 1·2 |
| | | Granite-gneiss (14) | Canada, etc. | 1·1 |
| 62·9–62·1 | 62·6 | Diorite (3) | California | 1·5 |
| 64·1–56·0 | 60·3 | Syenite (6) | N.Y. and Minn. | 1·0 |
| 57·9–49·6 | 53·1 | Phonolite (4) | Africa | 0·7 |
| | 47·6 | Gabbro-diorite (4) | California | 1·2 |
| 57·7–44·4 | 50·0 | Mostly mafic (24)[3] | Various[4] | 1·3 |
| 50·1–47·4 | 48·6 | Basalt | Michigan[5] | 0·8 |
| 50·4–46·0 | 47·4 | Basalt | Michigan[6] | 1·8 |
| | | Basalt | Michigan[7] | 2·6 |
| 54·7–33·4 | 42·8 | Ultramafic (6)[8] | U.S. and Newfoundland | 0·8 |

* Arsenic determinations in this and following tables by H. ONISHI.
[1] Four granites, 2 quartz monzonites, 1 monzonite, 2 granodiorites.
[2] Same as the preceding composite except for an additional sample.
[3] Nine gabbros, 1 norite, 4 diabases, 8 basalts, 1 peridotite, 1 pyroxenite.
[4] Eastern and western U.S. 13, Newfoundland 1, Africa 1, Antarctica 3, India 1, unspecified localities (probably U.S.) 5.
[5] Weighted composite of the Greenstone flow.
[6] Weighted composite of Kearsarge flow.
[7] Average of ten miscellaneous Michigan Keweenawan flows (Table 10).
[8] One peridotite, 1 dunite, 2 harzburgites, 1 bronzitite, 1 pyroxenite.

*Table 2. Arsenic in silicic volcanic rocks*

| *Sample* | As, *p.p.m.* |
|---|---|
| Felsite (probably intrusive), Bare Hill, Mich. | 3·4, 3·8 |
| Felsite, Mt. Houghton, Mich, lower half of mass | 5·5 |
| Felsite, Mt. Houghton, Mich., upper half | 3·0 |
| Rhyolite, Devils Track River, Cook Co., Minn. | 2·2 |
| Rhyolite, Cook Co., Minn. | 7·5 |
| Rhyolite, composite of 12 beach pebbles, 5 miles east of Grand Marais, Minn. | 3·6 |
| Rhyolite, overlying Endion Sill, Duluth, Minn. | 3·2 |
| Rhyolite porphyry, Great Palisades, Lake Co., Minn. | 6·0 |
| Rhyolite porphyry, 2·5 miles east of Grand Marais, Minn. | 3·3 |
| Rhyolite, White Pine, Nev. | 1·6 |
| Soda rhyolite (intrusive), West Texas | 4·0 |
| Quartz keratophyre, Marblehead, Mass. | 1·1 |
| Rhyolite, Birchy Island, Notre Dame Bay, Newfoundland | 1·6 |
| Rhyolite, West Indies | 0·7 |
| Liparite, Hattori, Ishikawa Pref., Japan | 2·3 |
| Liparite, Nishiyama, Yamagata Pref., Japan | 7·4 |
| Avg. | 3·5 |
| *Glasses* | |
| Obsidian (black), Obsidian Cliff, Yellowstone Park | 2·9 |
| Obsidian, locality unspecified | 5·3 |
| Rhyolitic obsidian, Clear Lake, Calif. | 8·7, 8·4 |
| Biotite rhyolitic pumice, Clear Lake, Calif. | 10·8, 10·8 |
| Rhyolitic obsidian, unknown locality | 2·9 |
| Volcanic glass, Ariz. | 4·6 |
| Volcanic glass, Ariz. | 12·2 |
| Volcanic glass, Ariz. | 8·1 |
| Volcanic glass, Ariz. | 3·8 |
| Perlite, Washington State | 2·0 |
| Perlite, Yutanaka, Nagano Pref., Japan | 4·8 |
| Pitchstone, Yutanaka, Nagano Pref., Japan | 4·1, 4·4 |
| Avg. | 5·9 |

*Table 3. Arsenic in granitic rocks*

| *Sample* | As, *p.p.m.* |
|---|---|
| *Minnesota* | |
| Hornblende granite ("St. Cloud Red"), Stearns Co. | 1·4 |
| Hornblende granite, Stearns Co. | 2·0 |
| Hornblende granite, Freedhem, Morrison Co. | 1·1 |
| Quartz monzonite, Rockville, Stearns Co. | 1·0 |
| Granite ("Mottled Venetian"), Stearns Co. | 1·6 |
| Porphyritic granite, Stearns Co. | 1·3 |
| Porphyritic granite, Stearns Co. | 0·8 |
| Biotite granite (coarse-grained), Benton Co. | 0·6 |
| Biotite granite (fine-grained), Benton Co. | 0·8 |
| Granite, red, Benton Co. | 1·1 |

*Table 3—continued*

| *Sample* | As, *p.p.m.* |
|---|---|
| *Minnesota (continued)* | |
| Granite, grey, Benton Co. | 0·9 |
| Granite porphyry (dike), Benton Co. | 1·1 |
| Aplite, Stearns Co. | 0·5 |
| Granodiorite, Stearns Co. | 2·3 |
| Granodiorite, Sherburne Co. | 1·0 |
| Granite porphyry, Sauk Rapids | 0·9 |
| Quartz monzonite, near Pierz | 0·8 |
| Quartz monzonite, Warman, old quarry | 0·0 |
| Quartz monzonite, Warman, new quarry | 0·6 |
| Quartz monzonite, northern Kanabec Co. | 0·7 |
| Granite, red, Lower Falls, Snake River, Kanabec Co. | 1·2 |
| Granite-gneiss, Morton | 1·0 |
| Avg. | 1·0 |
| *Other U.S. and Canadian localities* | |
| Granite, Chippewa Falls, Wis. | 0·5 |
| Granite, Graniteville, Mo. | 2·2 |
| Granite, Mo. | 3·7, 3·8 |
| Granite, Mine La Motte, Mo. | 1·7 |
| Granite (standard G–1), Westerly, R. I. | 1·0, 1·0 |
| Hornblende granite, Devils Slide, N.H. | 0·6 |
| Muscovite-biotite granite, Concord, N.H. | 2·8 |
| Hornblende granite, Rockport, Mass. | 1·3 |
| Alkalic granite, Quincy, Mass . | 1·3 |
| Muscovite-biotite granite, Mt. Airy, N.C. | 0·9 |
| Quartz monzonite, Boulder Co., Colo. | 0·6 |
| Muscovite granite, southern Ariz. | 0·4 |
| Granodiorite, Great Bear Lake, Canada | 3·7 |
| Avg. | 1·6 |
| *Japan, China, Africa* | |
| Granite, Masutomi, Yamanashi Pref., Japan | 7·6, 7·4 |
| Granite, Naegi, Gifu Pref., Japan | 1·2 |
| Granite, Asofu, Gifu Pref., Japan | 3·5 |
| Biotite granite, Mannari, Okayama Pref., Japan | 0·5 |
| Biotite granite, Nagano Pref., Japan | 6·5, 6·7 |
| Biotite granite, Gifu Pref., Japan | 1·7 |
| Biotite granite, Yamanoo, Ibaraki Pref., Japan | 0·5 |
| Hornblende granite, Kamitakara, Gifu Pref., Japan | 0·6 |
| Hornblende granite, Samekawa, Fukushima Pref., Japan | 1·0 |
| Granite porphyry, Minakami, Gumma Pref., Japan | 0·8 |
| Granodiorite, Sasahara, Fukushima Pref., Japan | 0·5 |
| Granite, China | 0·4 |
| Granite, Hong Kong | 4·2 |
| Porphyritic granodiorite, Hong Kong | 8·5 |
| Gneissic granite, Bambi Hills, Liberia | 1·5 |
| Hornblende granite (cassiterite-bearing), Sterkwater, Transvaal, Africa | 0·26% |
| Avg. excluding Sterkwater | 2·6 |
| Avg. of all | 1·7 |

*Table 4. Arsenic in intermediate rocks*

| *Sample* | As, *p.p.m.* |
|---|---|
| *United States* | |
| Augite andesite, Clear Lake, Calif. | 5·8 |
| Olivine andesite, Clear Lake, Calif. | 2·4 |
| Pyroxene rhyodacite, Clear Lake, Calif. | 5·8 |
| Olivine dacite, Clear Lake, Calif. | 2·9 |
| Hypersthene dacite, Clear Lake, Calif. | 2·0 |
| Biotite hornblende rhyodacite, Clear Lake, Calif. | 5·8, 5·8, 5·4 |
| Silicic pyroxene dacite, Clear Lake, Calif. | 5·4 |
| Andesite, Mt. Baker, Wash. | 2·3 |
| Andesite, Mt. Rainier, Wash. | 1·4 |
| Dacite, San Luis Obispo Co., Calif. | 1·8 |
| Mica dacite, Sunshine Canyon, Boulder Co., Colo. | 0·6 |
| Enstatite diorite, Santa Clara, Co., Calif. | 0·5 |
| Hornblende tonalite, Freedhem, Minn. | 0·8 |
| Hornblende tonalite (medium texture), Freedhem, Minn. | 0·8 |
| Augite syenite, Cook Co., Minn. | 1·7, 1·5 |
| Porphyritic syenite, Wausau, Wis. | 2·3 |
| Pulaskite, Fourche Mtn., Ark. | 3·1 |
| Avg. | 2·7 |
| *Localities outside U.S.* | |
| Taqui flow, Paricutin, Mex. | 1·1 |
| Zapico flow, Paricutin, Mex. | 1·0 |
| Andesite, West Indies | 0·6 |
| Andesite, West Indies | 1·8 |
| Dacite, Palau | 1·6 |
| Andesite, Yatsugatake, Nagano Pref., Japan | 1·1 |
| Augite andesite, Kumanmoto Pref., Japan | 0·5 |
| Augite andesite, Suwa, Nagano Pref., Japan | 1·0 |
| Pyroxene andesite, Yutanaka, Nagano Pref., Japan | 1·5 |
| Pyroxene andesite, Yakedake, Nagano Pref., Japan | 4·0 |
| Hornblende biotite andesite, Kamitakara, Gifu Pref., Japan | 2·9, 3·0 |
| Dacite (1952 lava), Myojin Reef, Izu, Japan | 4·5 |
| Diorite, Yamanashi Pref., Japan | 2·6 |
| Diorite, Ishikawa, Fukushima Pref., Japan | 1·0 |
| Quartz diorite, Miyamoto, Fukushima Pref., Japan | 0·6 |
| Quartz diorite, Minakami, Gumma Pref., Japan | 2·1 |
| Diorite, Miyamoto, Fukushima Pref., Japan | 1·4 |
| Gabbro diorite, Kansaka, Gifu Pref., Japan | 12·5, 13·4 |
| Gabbro diorite, Minano, Saitama Pref., Japan | 0·7 |
| Avg. | 2·3 |
| Avg. of all | 2·4 |
| Avg. of all except Kansaka gabbro diorite | 2·1 |

*Table 5. Arsenic in basalts and diabases*

| *Sample* | As, *p.p.m.* |
|---|---|
| *Minnesota* | |
| Basalt, dike, St. Cloud | 0·8 |
| Basalt, dike, St. Cloud | 0·7 |
| Basalt, dike, Duluth | 2·3, 2·3 |
| Basalt, overlying Puckwunge sandstone, NW 1/4 Sec. 20, T.49N.R.15 W., Duluth | 113, 27* |
| Diabase, Lester River Sill, (Schwartz No. 18), Duluth | 9·0 |
| Diabase, Lester River Sill (Schwartz No. 15), Duluth | 2·3 |
| Diabase, locality not known | 1·9 |
| Diabase, Grand Marais, barrier of harbour | 1·4 |
| Diabase, 3 miles east of Grand Marais | 1·8 |
| Basalt or diabase, Cook Co. | 0·7 |
| Basalt or diabase, Cook Co. | 0·8 |
| Basalt, Cook Co. | 0·8 |
| Porphyritic diabase or basalt (with visible pyrite), Cook Co. | 11·2† |
| Greenstone, Winton | 1·0 |
| Greenstone, near Ely | 8·8 |
| Avg. | 2·5 |
| *Other U.S. localities* | |
| Diabase, Interstate Park, Wis. | 1·4 |
| Diabase, Interstate Park, Wis. | 1·0 |
| Porphyritic diabase, Interstate Park, Wis. | 1·2 |
| Diabase, near Interstate Park, Wis. | 1·1 |
| Olivine diabase, Skrainka, Mo. | 0·7 |
| Diabase, Medford, Mass. | 0·8 |
| Basalt, Somerset Co., N.J. | 6·5 |
| Mica basalt, Franklin, N.J. | 1·8 |
| Diabase (standard W–1), Fairfax Co., Va. | 1·8, 1·8 |
| Olivine basalt, Jefferson Co., Colo. | 0·8 |
| Diabase basalt porphyry, Boulder Co., Colo. | 1·2 |
| Olivine basalt, Oregon | 1·0 |
| Olivine basalt, Oregon | 0·6 |
| Olivine basalt, Oregon | 0·6, 0·6 |
| Olivine basalt, Oregon | 0·9 |
| Olivine basalt, Oregon | 1·2 |
| Olivine basalt, Oregon | 0·6 |
| Olivine basalt, Oregon | 0·6 |
| Olivine basalt, Mt. St. Helens, Wash. | 5·5 |
| Olivine basalt, Clear Lake, Calif. | 2·0 |
| Picritic basalt, Terlingua-Solitario, Texas | 1·3 |
| Ultrabasic basalt, West Texas | 1·0 |
| Avg. | 1·5 |
| *Localities outside U.S.* | |
| Diabase porphyry, Mt. Etna, Sicily | 1·5 |
| Diabase, Kotaki, Niigata Pref., Japan | 2·0 |
| Diabase, Kamitakara, Gifu Pref., Japan | 1·4 |
| Diabase, Minakami, Gumma Pref., Japan | 1·0 |
| Basalt (Sept. 1950 lava), Miharayama, Oshima Volcano, Izu, Japan | 3·0 |
| Avg. | 1.8 |
| Avg. of all | 1·9 |

* Values for two different specimens from the outcrop. This specimen not included in average.

† Not included in average on the assumption that arsenic is mostly in the pyrite, and this was introduced after crystallization of rock.

*Table 6. Arsenic in gabbros and related rocks*

| *Sample* | As, *p.p.m.* |
|---|---|
| *Minnesota* | |
| Gabbro, above cement plant, Duluth | 3·6 |
| Gabbro, Fairmount Park, Duluth | 1·1 |
| Gabbro, Lookout Point, Duluth | 0·7 |
| Gabbro, base, Duluth | 1·0 |
| Gabbro, Bardon's Peak, Duluth | 1·8 |
| Gabbro, near Bardon's Peak, Duluth | 0·8 |
| Troctolite (banded), Bardon's Peak, Duluth | 0·3 |
| Troctolite, Duluth | 0·4 |
| Orthoclase gabbro, Duluth | 1·5 |
| Red rock, 13th Avenue, between 4th and 6th St., Duluth | 2·2 |
| Red rock, 5th St. and 21st Ave. W., Duluth | 5·6 |
| Red rock, 1st St. N. and about 12th Ave., Duluth | 1·8 |
| Gabbro (with Cu-Ni sulphides), near Ely | 0·2, 0·2 |
| Anorthositic gabbro, Lake Isabella | 1·0 |
| Anorthosite, Split Rock | 1·1 |
| Actinolite gabbro, Mora | 0·5 |
| Hornblende norite, Stearns Co. | 0·3 |
| Hornblende norite (?), probably hornfels, Stearns Co. | 0·8 |
| Avg. | 1·4 |
| *Other U.S. localities* | |
| Gabbro, Charlottesville, Va. | 0·8 |
| Hornblende gabbro, near Shelby, N.C. | 1·7 |
| Olivine gabbro, White Mtn., Park Co., Wyo. | 1·3 |
| Olivine gabbro, Cripple Creek, Colo. | 0·8 |
| Norite, Essex Co., N.Y. | 1·3 |
| Avg. | 1·2 |
| *Localities outside U.S.* | |
| Norite, Sudbury, Ontario | 3·8 |
| Hornblende gabbro, Humacao, Puerto Rico | 0·6 |
| Gabbro, No. Transvaal, Africa | 0·6 |
| Gabbro, Great Dyke, Africa | 0·6 |
| Gabbro, Great Dyke, Africa | 0·7 |
| Gabbro, Bushveld Complex, Africa | 2·8 |
| Gabbro, S.E. Bushveld Complex, Africa | 2·4 |
| Gabbro, La Mota Mtn., Tascotal Quadrangle, Texas | 1·3 |
| Avg. | 1·6 |
| Avg. of all | 1·4 |

*Table 7. Arsenic in ultramafic rocks and serpentines*

| *Sample* | As, *p.p.m.* |
|---|---|
| Pyroxenite, Lewis Hills, Newfoundland | 0·5 |
| Pyroxenite, Webster, N.C. | 0·3 |
| Hornblende pyroxenite, Humacao, Puerto Rico | 0·3 |
| Bronzitite, Beartooth Mtns., Mont. | 0·8 |
| Bronzitite | 1·3 |
| Peridotite, Syracuse, N.Y. | 0·9 |
| Peridotite, Euclid, N.Y. | 3·0 |
| Peridotite, Bird River, Can. | 0·9 |
| Peridotite | 1·5 |
| Dunite, Balsam, N.C. | 0·4 |
| Dunite, N.C. | 0·6 |
| Dunite, Lewis Hills, Newfoundland | 0·8 |
| Dunite | 0·4 |
| Feldspathic dunite, Lewis Hills, Newfoundland | 0·5 |
| Serpentinized dunite, Venezuela | 0·5 |
| Harzburgite, Beartooth Mtns., Mont. | 2·1 |
| Harzburgite, Lewis Hills, Newfoundland | 0·8 |
| Serpentinized harzburgite | 0·5 |
| Lherzolite, Baltimore, Md. | 1·2 |
| Avg. | 0·9 |
| Serpentine, Yearlying Head, Llano region, Texas | 1·8, 2·0 |
| Serpentine, Gillespie Co., Texas | 3·6 |
| Serpentine, San Francisco, Calif. | 1·3 |
| Serpentine, Hoboken, N.J. | 0·8 |
| Serpentine, locality unknown (probably U.S.) | 6·2 |
| Serpentine, Kamitakara, Gifu Pref., Japan | 15·3, 15·8 |
| Serpentine, Yorii, Saitama Pref., Japan | 11·4 |
| Serpentine, Miyamori, Iwate Pref., Japan | 6·6 |
| Serpentine, Machiya, Ibaraki Pref., Japan | 1·0 |
| Serpentine glass | 1·3 |
| Avg. | 5·0 |
| Kimberlite, So. Africa | 3·5 |

samples may be found in an earlier paper on the geochemistry of molybdenum (Kuroda and Sandell, 1954). The frequency distribution of arsenic in silicic, mafic, and ultra-mafic rocks is shown in Fig. 1.

The arsenic values of some miscellaneous minerals are collected in Table 8. The arsenic contents of the component minerals of a few igneous rocks are given in Table 9. The component minerals were separated by hand picking, bromoform flotation, and magnetically.

Tables 10–13 contain data on the arsenic content of a number of series of genetically related rocks.

*Summary and discussion of the findings*

*General.* Averages and standard deviations of the mean for various rock types are as follows (the number of samples are given in parentheses):

| | As, *p.p.m.* | |
|---|---|---|
| Silicic volcanic rocks | | |
| Rhyolites, felsites, liparites (16) | 3·5 ± 0·5 | |
| Glasses (12) | 5·9 ± 0·9 | |
| Granitic rocks | | |
| Weighted average of 6 composites (63) | 1·4 | 1·5 |
| Individual samples (50)* | 1·7 ± 0·3 | |
| Intermediate rocks (36) | 2·4 ± 0·4 | |
| Basalts and diabases | | |
| Individual samples (40)† | 1·9 ± 0·3 | 2·0 |
| Average of 12 Michigan basic flows (Table 1) | 2·4 | |
| Gabbros (31) | 1·4 ± 0·2 | |
| Ultramafic rocks | | |
| Peridotites, dunites, etc. (19) | 1·0 ± 0·2 | |
| Serpentines (10) | 2·8‡ | |

* A cassiterite-bearing African granite with 0·26 per cent As not included.
† Two Minnesota basalts with 70 p.p.m. (average) and 11·2 p.p.m. As not included.
‡ Two samples with 15·6 and 11·4 p.p.m. As are excluded. If these are included, the average is 5·0 p.p.m.

The amounts and the distribution patterns are much the same for granitic rocks, intermediate rocks, basalts and diabases, and gabbros. The granitic average (1·5 p.p.m.) does not differ enough from the basaltic and gabbroic averages (2·0, 1·4 p.p.m.) to justify a claim for a significant difference in the arsenic contents of these contrasting rocks. Rhyolitic rocks and silicic glasses are higher in arsenic than other common rock types, the difference being most pronounced for the glasses. There is some indication that the intermediate volcanic rocks tend to be somewhat higher than basalts and diabases, but the number of samples is too small to carry much conviction. Ultramafic rocks (excluding serpentines) seem to be a little lower in arsenic than the mafic rocks.

The arsenic content of the lithosphere may be approximated as 2 p.p.m., based on the averages for about 200 granitic rocks, basalts, and gabbros. An average as

low as 1 p.p.m. appears unlikely. On the other hand, the occasional samples of very high arsenic content may raise the question whether the true average may not be greater than 2 p.p.m. On the whole we are inclined to discount the importance of occasional high-arsenic samples. An element, such as arsenic, with considerable mobility may be found localized in the upper levels of the crust in concentrations

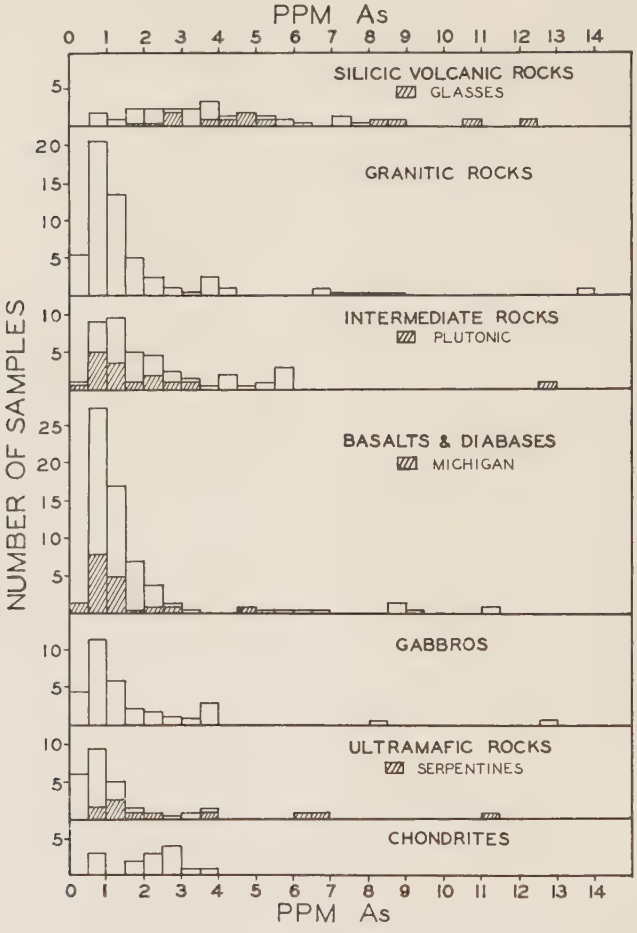


Fig. 1. Frequency distribution of arsenic in igneous rocks and chondrites.

not typical of the crust as a whole. Analysis of a larger number of samples of the common igneous rocks might conceivably yield an average of, say, 3 p.p.m. A value as high as 5 p.p.m. As (Clarke and Steiger) seems improbable. Only 12 per cent of the granitic rocks and 11 per cent of the basaltic rocks and gabbros analyzed in the present work exceeded 5 p.p.m. As.

Both from the distribution of arsenic in common rock types and from the arsenic content of the component minerals of igneous rocks, it is clear that the element does not exclusively or principally follow any one of the major constituents. In part it must follow silicon, as shown by its presence in quartz and agate. The

*Table 8. Arsenic in miscellaneous minerals*

| *No.* | *Mineral* | As, *p.p.m.* |
|---|---|---|
| 1 | Feldspar, pegmatitic, Kanabec Co., Minn. | 0·7 |
| 2 | Feldspar, vein in granite, Kanabec Co., Minn. | 0·7 |
| 3 | Bytownite, Crystal Bay, Minn. | 1·3 |
| 4 | Amazonite, Mont Anpanobe, Madagascar | 1·2 |
| 5 | Quartz, vein in slate, Thomson, Minn. | 0·4 |
| 6 | Quartz | 0·5 |
| 7 | Quartz | 0·5 |
| 8 | Quartz } locality and type not known | 0·6 |
| 9 | Quartz | 1·3 |
| 10 | Quartz | 1·3 |
| 11 | Agate, gray, Encampment Forest, Lake Superior, Minn. | 1·1 |
| 12 | Agate, red-brown, composite of 3, Lake Superior, Minn. | 3·7 |
| 13 | Agate, blue-grey, near Alpine, Texas | 1·2 |
| 14 | Magnetite-ilmenite sand, Cook Co., Minn. | 10·6 |
| | Magnetic fraction | 6·4 |
| | Non-magnetic fraction | 16·4 |
| 15 | Magnetite (with ilmenite), strongly magnetic fraction of gabbro at Lookout Point, Duluth | 5·5[1] |
| 16 | Magnetite (with ilmenite), strongly magnetic fraction of anorthositic gabbro, Lake Isabella, Minn. | 3·8[1] |
| 17 | Magnetite (with ilmenite), strongly magnetic fraction of basalt, Duluth | 4·7[1] |
| 18 | Magnetite (with ilmenite), strongly magnetic fraction of diabase, Taylors Falls, Minn. | 2·7[1] |
| 19 | Pyroxene, pegmatitic phase of gabbro, Duluth, Minn. | 0·8 |
| 20 | Pyroxene, Libby, Mont. | 0·2 |
| 21 | Hypersthene. West Texas | 0·5 |
| 22 | Diallage, Sonoma Co., Calif. | 0·9 |
| 23 | Amphibole, India | 1·1 |
| 24 | Almandite, Gore Mtn., N.Y. | 0·4 |
| 25 | Barite, vein in Endion Sill, Duluth | 0·4 |
| 26 | Calcite, in basalt, near Alpine, Texas | 0·0 |
| 27 | Pyrite, in slate, Thomson, Minn. | 450 |

[1] Because of limited sample, error may be ±30 per cent.

ionic radii (Ahrens) of $As^{+3}$ (0·58 Å) and $As^{+5}$ (0·46) are sufficiently similar to the radius of $Si^{+4}$ (0·43) to make ionic substitution a possibility, particularly with quinquevalent arsenic. The valence state of arsenic in magmas seems to be uncertain. Presumably arsenic is present chiefly in the trivalent form, particularly in magmas having a low $Fe^{+3}/Fe^{+2}$ ratio, but the presence of some $As^{+5}$ does not seem to be excluded. For quartz, a substitution of the type $(Si, M^{+3})(Si, As^{+5})O_4$ immediately comes to mind, where $M^{+3}$ might be aluminium or other trivalent cation ($As^{+3}$?). However, for five quartzes in Table 8 (Nos. 6–10), whose content of Ti, Fe, Al, and Mn had been determined, no relation between As and Al or the other trace elements was apparent.

Replacement of $Al^{+3}$ (0·51 Å) by arsenic should be possible, and the occurrence

*Table 9. Arsenic and molybdenum in component minerals of igneous rocks*

| *Rock* | *Mineral* | *% of rock* | Mo, *p.p.m.* | As, *p.p.m.* | *P.p.m.* As *contributed to rock* |
|---|---|---|---|---|---|
| Hornblende granite, Stearns Co., Minn. | K-feldspar | 68 | 0·9 | 1·7 | 1·2 |
| | Plagioclase | 15 | 0·3 | 1·4 | 0·2 |
| | Hornblende + biotite | 7 | 8·7 | 10·3 | 0·7 |
| | Quartz | 10 | 0·0 | 1·3 | 0·1 |
| | | | | total | 2·2 (2·0 by direct analysis) |
| Quartz monzonite, Rockville, Stearns Co., Minn, | Microcline | 35 | 0·4 | 0·8 | 0·3 |
| | Plagioclase (An 28) | 35 | 2·5 | 0·8 | 0·3 |
| | Biotite | 7 | 3·1 | 1·4 | 0·1 |
| | Quartz | ~20 | 0·1 | 0·9 | 0·2 |
| | | | | total | 0·9 (1·0 by direct analysis) |
| Granite, Devils Slide, N.H. | Feldspar (chiefly perthite) | 70 | | | |
| | Amphibole (sodic) | 5 | 1·8 | 2·3 | 0·1 |
| | Quartz | 25 | | | |
| | | | | total by direct analysis | 0·6 |
| Hornblende tonalite, Freedhem, Minn. | Feldspar | 50 | 0·5 | 0·8 | 0·4 |
| | Heavy fraction (mostly hornblende + biotite) | 50 | 1·2 | 1·0 | 0·5 |
| | | | | total | 0·9 (0·8 by direct analysis) |
| Augite syenite, Cook Co., Minn. | Light fraction (mostly feldspar) | 73 | 1·2 | 1·1 | 0·8 |
| | Non-magnetic heavy fraction (pyroxene, amphibole, ilmenite, epidote) | 20 | 4·3 | 2·4 | 0·5 |
| | Magnetic fraction | 7 | 3·7 | 5·8 | 0·4 |
| | | | | total | 1·7 (1·6 by direct analysis) |

*Table 9—continued*

| *Rock* | *Mineral* | *% of rock* | Mo, *p.p.m.* | As, *p.p.m.* | *P.p.m.* As *contributed to rock* |
|---|---|---|---|---|---|
| Gabbro, Duluth, near Bardon's Peak | Plagioclase | ~80 | 0·4 | 2·1 | 1·7 |
| | Non-magnetic heavy fraction (about one-half amphibole, remainder epidote, pyroxene, ilmenite with magnetite, etc.) | ~18 | 1·6 | 5·0 | 0·9 |
| | Magnetite (with ilmenite) | 2·5 | 16 | 41 | 1·0 |
| | | | | total | 3·6 (3·6 by direct analysis) |
| Gabbro, Duluth, Fairmount Park | Plagioclase | 80–85 | 0·6 | 1·1 | 0·9 |
| | Non-magnetic heavy fraction (mostly pyroxene, some ilmenite with magnetite) | 15–20 | 1·6 | 1·3 | 0·2–0·3 |
| | Magnetite (with ilmenite) | 1 | — | — | — |
| | | | | total | ~1·2 (by direct analysis = 1·1) |

of arsenic in feldspars and other alumino-silicates is not surprising. In addition, arsenic can doubtless substitute for $Fe^{+3}$ (0·64 Å) and $Ti^{+4}$, as shown by its presence, sometimes in comparatively large amounts, in magnetite and ilmenite (Tables 8 and 9). Sulphide inclusions in these and other minerals are not likely to account for much arsenic. Although apatite has not been separated from our igneous rocks and its arsenic content determined, indirect evidence makes it improbable that this mineral contributes more than a minor fraction of the total arsenic. For igneous rocks as a whole, the feldspars probably account for one-half or more of the total arsenic.

In Table 9 the molybdenum content of the component minerals (available from earlier work, Kuroda and Sandell, 1954) has been included for comparison with the arsenic content. Except for quartz, the two elements tend to vary similarly from one mineral to another, but the variation is greater for molybdenum. Since molybdenum is believed to replace Al, $Fe^{+3}$, $Ti^{+4}$, and possibly Si, in rock-forming minerals, qualitative similarity in behaviour of the two elements

*Table* 10. *Arsenic in Keweenawan rocks of Michigan*

| *Broderick's No.* | As, *p.p.m.* | $FeO/Fe_2O_3$ |
|---|---|---|
| *Greenstone Flow* | | |
| 3132 (top) | 2·8 | |
| 3134 | 1·1 | |
| 3136 (doleritic zone) | 1·3 | |
| 3138 | 0·7 | |
| 3140 (doleritic zone) | 0·7, 0·7 | |
| 3142 | 1·1 | |
| 3144 | 0·9 | |
| 3146 | 0·5 | |
| 3148 | 0·7 | |
| 3150 | 0·4 | |
| 3152 | 0·6 | |
| 3154 (bottom) | 0·6 | |
| Weighted composite of above | 0·8 | 2·6 |
| *Kearsarge Flow* | | |
| 3112 (top) | 2·4 | |
| 3113 | 4·8 | |
| 3115 | 1·0 | |
| 3117 | 1·2 | |
| 3119 | 1·5 | |
| 3121 | — | |
| 3123 (bottom) | 0·7 | |
| Weighted composite of above | 1·8 | 1·3 |
| *Miscellaneous Keweenawan* | | |
| 3091 Melaphyre | 1·0 | 1·2 |
| 3095 Ophitic | 0·9 | 1·8 |
| 3103 Glomeroporphyrite | 2·3 | 1·1 |
| 3104 Melaphyre | 2·2 | 1·2 |
| 3106 Melaphyre | 1·3 | 1·3 |
| 3110 Glomeroporphyrite | 0·7 | 0·5 |
| 3127 Melaphyre | 3·0 | 1·0 |
| 3129 Melaphyre | 1·3 | 0·9 |
| 3156 Felsite (intrusive) | 3·4, 3·8 | 0·11 |
| 3157 Felsite | 5·5 | 0·11 |
| 3159 Felsite | 3·0 | 0·12 |
| 3161 Gabbro aplite | 1·6 | 1·6 |
| 3163 Gabbro, intermediate | 8·0, 8·2 | 1·3 |
| 3166 Gabbro, basic | 3·0 | 1·3 |
| 3169 Felsite porphyrite | 4·0 | 0·3 |
| 3170 Porphyrite | 9·2, 9·8 | 0·13 |

is not unexpected. However, when whole rocks are compared, no particular relationship between arsenic and molybdenum is evident, as if the variation from one magma to another is not generally similar for the two (Table 13).

A Minnesota gabbro containing copper and nickel sulphides (Table 6) showed only 0·2 p.p.m. As, the lowest of any gabbro examined. In this sample at least, arsenic shows no tendency to enter magmatic sulphides.

As far as the available data go, there appears to be little tendency for arsenic to be enriched in alkalic rocks.

One-hundred-mesh powders of three igneous rocks with high arsenic contents were treated with water and acids, and arsenic was determined in the successive fractions:

| | *Sheep Canyon basalt* (*Table* 13) | *Petrick granite* (*Table* 12) | *Porphyrite No.* 3170 (*Table* 10) |
|---|---|---|---|
| Water | 1·2 p.p.m. As | 0·4 p.p.m. As | 0·7 p.p.m. As |
| Cold 1 : 1 HCl | 16·2 | 0·9 | 3·4 |
| Hot conc. $HNO_3$ | 14·0 | 7·4 | 1·3 |
| Sum | 31·4 | 8·7 | 5·4 |
| Total arsenic in rock by direct analysis | 32, 33 | 13·6, 14·0 | 9·8, 9·2 |

The full meaning of these results is uncertain. Possibly they could be interpreted as indicating the presence of some arsenic in interstitial material. In two of the rocks (Petrick granite and Michigan porphyrite) 37 and 43 per cent of the total arsenic was unextracted by the acid treatment, and these amounts at least are probably present in the interior of silicate or oxide minerals. Doubtless some arsenic was leached from, or dissolved with, the silicate or oxide, so that more than this was originally present in the silicate or other minerals. The Michigan porphyrite is known to contain much hematite, and it is perhaps not surprising that it yielded two and one-half times as much arsenic to cold dilute hydrochloric acid as to hot concentrated nitric acid. The Texas basalt yielded practically all its arsenic to the acids. A small amount of arsenic was extracted from all three rocks by water. Perhaps some of this comes from the slight attack of the silicate; liquid inclusions might furnish a portion.

*Michigan Keweenawan.* Arsenic was determined in the basaltic Greenstone and Kearsarge flows and the miscellaneous Keweenawan rocks (Table 10) studied by Broderick (1935). The most interesting feature of the 1600-feet thick Greenstone flow is the presence in its upper half of coarse-grained "doleritic" facies (Nos. 3136 and 3140), considered by Broderick to result from the concentration of volatiles. Na, K, Fe, Ti, P, Mn, S, Cu, and Mo are present in greater than average amounts in these zones, whereas Al and Mg are below average. Arsenic does not show a clear tendency to be concentrated in the doleritic zones; one

*Table* 11. *Arsenic in diabasic and red rock facies of Endion Sill*

| *Sample* | $SiO_2$ % | $Na_2O$ % | $K_2O$ % | As, *p.p.m.* |
|---|---|---|---|---|
| Ophitic diabase (Schwartz and Sandberg No. 1) | 47·3 | 2·5 | 0·8 | 4·7, 4·3 |
| Diabase at first gradation to red rock (No. 3) | 52·4 | 3·0 | 2·4 | 3·0, 3·0 |
| Intermediate red rock (No. 4) | 61·5 | 3·3 | 4·3 | 1·7, 1·4, 1·8 |
| Red rock within a few feet of rhyolite contact (No. 6) | 61·1 | 3·4 | 4·1 | 9·4 |
| Rhyolite (No. 7) (roof of sill) | 75·5 | 3·3 | 5·2 | 3·2 |

*Table* 12. *Arsenic in granites of Llano region, Texas*

| *Sample* | $SiO_2$, % | As, *p.p.m.* |
|---|---|---|
| Town Mountain (quartz monzonite) | 68·2 | 1·3 |
| Petrick | 71·9 | 13·6, 14·0 |
| Cassaday | 72·1 | 0·5, 0·7 |
| Granite Mountain | 73·0 | 1·0, 1·2 |
| Llanite (granite porphyry) | 75·2 | 0·7, 0·7 |
| Bear Mountain | 76·8 | 0·9, 0·9 |
| Petrick aplite | 76·7 | 1·6, 1·6 |

*Table* 13. *Arsenic and molybdenum in West Texas rocks*

| *Sample* | $P_2O_5$, % | $SiO_2$, % | As, *p.p.m.* | Mo, *p.p.m.* |
|---|---|---|---|---|
| Sheep Canyon basalt | 2·99 | 44·3 | 0·7, 0·7 | 1·2 |
| Sheep Canyon basalt | 0·87 | 45·7 | 32, 33 | 1·2 |
| Elephant Mountain basalt | 0·96 | 46·0 | 0·6 | 0·9 |
| Cottonwood Springs basalt | 1·97 | 46·9 | 0·9 | 2·3 |
| Cottonwood Springs basalt | 1·81 | 48·1 | 1·6 | 2·5 |
| Butcherknife Hill basalt | 1·10 | 48·5 | 1·2 | 3·2 |
| Buck Hill syenite | | 61·0 | 1·4 | 6·4 |
| Potato Hill andesite | | 61·5 | 1·4 | 0·9 |
| Crossen trachyte | | 71·2 | 4·2 | 6·2 |
| Mitchell Mesa rhyolite | | 78·8 | 5·4 | 0·6 |
| Pruett tuff | | 69·7 | 1·7 | 0·3 |
| Duff tuff | | 70·6 | 3·8 | 0·2 |

(3136) is slightly higher than the average of the flow in arsenic, the other (3140) is about average. On the other hand, the uppermost sample (3132), representing the upper 116 feet of the flow, is definitely higher in arsenic than the others. This sample is also the highest in S (0·9 per cent); for the other samples there is no correlation of arsenic and sulphur. No relation is apparent between arsenic and any major or minor constituent. Perhaps escape of arsenic from the lava has obscured relations that might otherwise exist.

The highest concentration of arsenic in the 165-feet Kearsarge flow is found in the fine-grained trap (3113), representing the 12 to 23-feet depth, below the amygdaloidal top. This sample also shows higher than average amounts of Na, K, Fe, Ti, P, S, Mn, and Cu, the concentration of which is attributed to volatile transfer by Broderick. In both the Kearsarge and Greenstone flows there appears to be a general tendency for arsenic to occur in larger amounts in the upper halves of the flows.

Ten samples under miscellaneous Keweenawan in Table 10 (3091-3129, 3169, and 3170) represent basaltic flows and provide an opportunity for tracing a possible trend of arsenic with differentiation within the earth's crust. Nos. 3091–3129 are each drill-core composites obtained by sampling the cores at intervals along their entire length through the flows. Nos. 3169 and 3170 are composites from outcrops sampled across the flow. The outcrops are described by Broderick as weathered, and he states that the high normative hematite content of these samples is probably due to weathering. In Fig. 2 the arsenic contents of the ten basaltic flows, together with the weighted average of the Greenstone and Kearsarge flows, are plotted against silica. A general tendency for arsenic to rise with silica is apparent, and it is tentatively concluded that the processes increasing the silica content of the flow-magmas also tend to increase the arsenic content. The anomalously high arsenic content of No. 3170 is very probably related to the high $Fe_2O_3$ content of this sample (12·8 per cent $Fe_2O_3$, $FeO/Fe_2O_3 = 0{\cdot}13$). If the low $FeO/Fe_2O_3$ ratio is due to weathering, adsorption of arsenic on ferric oxide or hydrous ferric oxide is a possibility; if it is due to oxidation by volatiles, these may have introduced arsenic. No. 3169, with the second highest arsenic content (4·0 p.p.m.) of the twelve samples, also shows a rather low (0·28) $FeO/Fe_2O_3$ ratio.

The Keweenawan felsites (3156, 3157, 3159) have more arsenic than the basalts on the average, but the increase with silica content is not as great as extrapolation of the trend in Fig. 2 would indicate.

The three facies of the Mt. Bohemia gabbro (3161, 3163, 3166) have widely varying arsenic contents not correlatable with the chemical composition.

*Duluth gabbro.* Systematic sampling of the mass of the Duluth gabbro has not been carried out, but it appears that the typical gabbro contains about 1 p.p.m. As (Table 6). A specimen with 3·6 p.p.m. As contains amphibole and epidote, and is not typical. Three samples of red rock of the gabbro have 2·2, 5·6, and 1·8 p.p.m. As, and another similar differentiate (from Cook Co., Minn.), given the field name augite syenite, has 1·6 p.p.m. There is thus some evidence for an increase of arsenic in the red rock, but the difference is not marked, on the whole. Arsenic thus differs from molybdenum, which shows a consistent and marked rise in the

red-rock facies. Anorthosite and anorthositic gabbro do not differ significantly from typical gabbro in arsenic content.

*Endion sill.* This 1200-feet diabase sill, in the city of Duluth, is characterized by an upper silicic "red rock" facies (granophyre), attributed by Schwartz and Sandberg (1940) to differentiation of sill magma. Arsenic does not vary in any simple way through the sill (Table 11), nor is there any correlation between arsenic and the alkali metals or silica. Arsenic is markedly concentrated in the red rock immediately adjacent to the rhyolite roof of the sill.

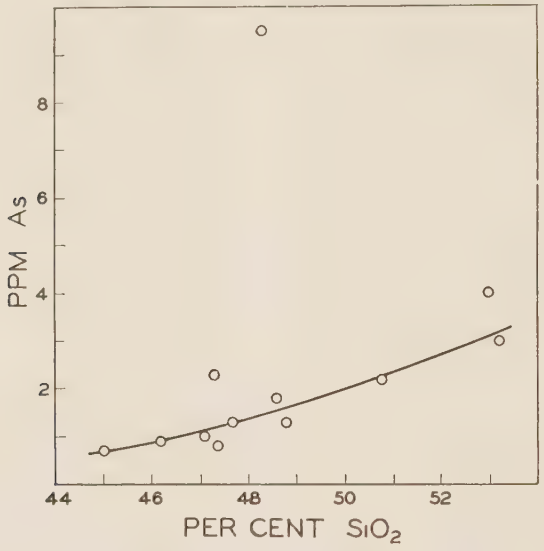


Fig. 2. Arsenic as a function of the silica content in basic Keweenawan flows of upper Michigan. Weighted composites of Greenstone and Kearsarge flows included.

*Granites of the Llano region, Texas.* These granites are regarded as a portion of a rock series representing differentiation through fractional crystallization (Goldich and Elms, 1949). With the exception of the Petrick granite, the group is rather uniform in arsenic content, and similar to other granites (Table 12). The reason for the high arsenic of the Petrick is not known; there is nothing in the bulk analysis to suggest abnormal composition. No relation between arsenic and the silica content of these granites is evident.

*West Texas.* A series of rocks from Buck Hill quadrangle in west-central Brewster County, described by Goldich and Elms (1949), were analyzed for arsenic (Table 13). The basalts have alkalic affinities. With the exception of one sample having abnormally high arsenic, these basalts do not differ from basalts of other regions in arsenic content. The rhyolite and trachyte show relatively much arsenic, in seeming accordance with the tendency of arsenic to rise in volcanic silicic rocks. The syenite contains about an average amount of arsenic. There is no evidence from this series that arsenic tends to be especially associated with the alkalies, in contrast to the behaviour of molybdenum.

The basalt with 32 p.p.m. As has an appreciably lower $FeO/Fe_2O_3$ ratio than the other basalts, namely 0·93 as compared to 2·0, 3·2, 1·9, 2·0, and 2·2.

The basalts of the series are all high in phosphorus, but apparently the apatite makes little contribution to the arsenic content. In this connection it may be noted that the magmatic apatite of the Kola Peninsula is very low in arsenic, with a range from 0·7 to 2·4 p.p.m. in eleven samples; however, the pneumatolytic apatite of Jumilla, Spain, contains 0·22 per cent As (*Gmelins Handbuch*, 1952, p. 17).

### B. *Sedimentary rocks*

In addition to the data in Table 14, we have arsenic values for shale composites:

| *Composite* | *Colour* | C, % | S, % | As, *p.p.m.* | Mo, *p.p.m.* |
|---|---|---|---|---|---|
| 14 Japanese Paleozoic shales (Minami, 1935) | light grey | — | 0·12 | 5·8 | 0·5 |
| 10 Japanese Mesozoic shales (Minami, 1935) | light grey | — | 0·20 | 6·7 | 2·9 |
| 36 European Paleozoic shales (Noll, 1934) | dark grey | 1·9 | 0·32 | 17·7 | 4·5 |

Shales are clearly richer in arsenic than igneous rocks, on the average. In this respect, arsenic is similar to molybdenum and various other heavy metals. Shales containing sulphides and carbonaceous matter tend to be high in arsenic. The presence of arsenic in sedimentary iron sulphides is well known. Arsenic is likely to be present also in adsorbed form on iron oxides, clay minerals, etc., in shales. A reducing environment is favourable for the accumulation of arsenic, but there are exceptions. Thus a vanadiferous shale from Idaho (Table 14) contains only 0·3 p.p.m. As (but 87 p.p.m. Mo). Possibly at very low oxidation potentials $AsH_3$ can form and escape. Also in this connection it may be recalled that micro-organisms can produce volatile organo-arsenic compounds (Challenger *et al.*, 1933).

Because of the strong variation of arsenic among shales, it is not possible to obtain a precise average from the present data. The weighted average of the three composites above, based on sixty European and Japanese shales, is 13 p.p.m. The average of twenty-nine individually analyzed samples in Table 14, mostly from North America, is 12 p.p.m. An average of 10 p.p.m. might be too high because of undue representation of samples rich in organic matter and sulphides. However, few samples in Table 14 contain less than 5 p.p.m. As, so that an average smaller than this is unlikely. Probably the average lies in the range 5–15 p.p.m., and we may give the most reasonable figure as $10 \pm 5$ p.p.m. As.

Arsenic is found in limestone only in small amounts, except when pyrite or carbonaceous material is present. An average of 1–2 p.p.m. probably will not be wide of the mark.

*Table* 14. *Arsenic in sedimentary rocks*

| *Sample* | As, *p.p.m.* |
|---|---|
| *Shale and clay* | |
| Vanadiferous shale, Paris-Bloomington district, Idaho | 0·3, 0·3 |
| Calcareous shale, Windy Creek area, Alaska | 14·7, 14·6 |
| Calcareous shale, Windy Creek area, Alaska | 20·8 |
| Calcareous shale, Windy Creek area, Alaska | 9·4 |
| Organic shale, Katella area, Alaska | 8·3 |
| Cason shale, Searcy Co., Ark. | 16·0 |
| Shale, Sawyer Quadrangle, N.D. | 14·6 |
| Shale, red, Aroostook Co., Maine | 3·2 |
| Shale or siltstone, Bad Lands, S.D. | 7·5 |
| Shale (Dresbach, Cambrian), Interstate Park, Wis. | 8·4 |
| Shale, green, Interstate Park, Wis. | 4·1 |
| Shale, yellow, Interstate Park, Wis. | 5·6 |
| Shale, pyritic phase, Interstate Park, Wis. | 16·2 |
| Decorah shale, Goodhue Co., Minn. | 6·8 |
| Decorah shale, Goodhue Co., Minn. | 10·0 |
| Decorah shale, St. Paul, Minn. | 5·8 |
| Decorah shale, St. Paul, Minn. | 4·9 |
| Glenwood shale, upper half, Columbia Heights, Minn. | 0·8 |
| Glenwood shale, lower half, Columbia Heights, Minn. | 1·0 |
| Glacial lake clay, Carlton Co., Minn. | 5·7 |
| Glacial lake clay, Carlton Co., Minn. | 8·2 |
| Residual clay, Redwood Falls, Minn. | 2·2 |
| Clay (Cretaceous), Morrison Co., Minn. | 2·0 |
| Clay (Cretaceous), Morrison Co., Minn. | 3·0 |
| Shale, green, Rochester, N.Y. | 22·4 |
| Shale, calcareous, Livingston Co., N.Y. | 6·8 |
| Shale, arenaceous, Green Co., N.Y. | 24·4 |
| Shale, carbonaceous, Green Co., N.Y. | 6·0 |
| Shale, bituminous, Le Roy, N.Y. | 59 |
| Shale (Mesozoic), Kamitakara, Gifu Pref., Japan | 9·3 |
| Shale (Tertiary), Yokote, Akita Pref., Japan | 2·6 |
| Shale, Itsukaichi, Tokyo, Japan | 12·7 |
| Shale, Kawai, Gifu Pref., Japan | 30·5 |
| Oil shale (tasmanite), near Latrobe, Tasmania | 6·5 |
| Bentonite, Gillette, Wyo. | 2·6 |
| *Limestone and dolomite* | |
| Limestone, Platteville, Columbia Heights, Minn. | 1·4 |
| Limestone, Platteville, Columbia Heights, Minn. | 2·8 |
| Dolomite, Oneota, Hastings, Minn. | 0·6 |
| Dolomite, Red Wing, Minn. | 0·6 |
| Dolomitic limestone, Kasota, Minn. | 1·3 |
| Dolomite (base of upper Cambrian), Taylors Falls, Minn. | 2·1 |
| Limestone, oolitic, Bedford, Ind. | 0·6 |
| Dolomitic limestone, Knoxville, Tenn. | 0·5 |
| Limestone, argillaceous, Trenton Falls, N.Y. | 0·8, 0·7 |

*Table* 14 (*continued*)

| *Sample* | As, *p.p.m.* |
|---|---|
| Dolomitic limestone, Rochester, N.Y. | 1·9 |
| Limestone, coral, Le Roy, N.Y. | 1·1 |
| Limestone, gray, Onondaga Co., N.Y. | 14·5 |
| Limestone, Concrete, Colo. | 0·5 |
| Limestone, Ruth, Nev. | 0·7 |
| Chalk, Dover, England | 0·3 |
| Limestone, Mt. Lebanon, Syria | 1·3 |
| Manganese-iron carbonate concretion, Chamberlain, S.D. | 20·1 |
| HCl-soluble portion | 18·2 |
| HCl-insoluble portion | 1·9 |
| *Sandstone* | |
| St. Peter sandstone, Minneapolis, Minn., digested with HCl and $HNO_3$ | 0·6 |
| St. Peter sandstone, Minneapolis, Minn., washed with HCl | 1·0 |
| Impure sandstone, Marine, Minn. | 1·3 |
| St. Lawrence sandstone, near Stillwater, Minn. | 1·8 |
| Glauconitic sandstone, near Stillwater, Minn. | 1·6 |
| Cambrian sandstone, Interstate Park, Wis. | 1·0 |
| *Miscellaneous* | |
| Chert, in Oneota dolomite, Hastings, Minn. | 0·9 |
| Flint, in Mitchell Mesa rhyolite, near Alpine, Texas | 2·9 |
| Glauconite, Mason Co., Texas | 8·2 |
| Glauconite, Onisakatoge, Yamagata Pref., Japan | 1·8 |
| Bauxite, Demerara, British Guiana | 4·5 |
| Phosphate rock (pebble phosphate), Brewster, Fla. | 2·3 |

*Table* 15. *Arsenic in deep-sea deposits*

| *Sample* | *Location* | *Depth* (*m*) | As, *p.p.m.* |
|---|---|---|---|
| Muddy sand | Sea of Japan 41°44′28″N 130° 1′46″E | 226 | 14·0 |
| Blue mud | Sea of Japan 41°34′18″ 130°26′12″ | 2791 | 7·6 |
| Red clay | Sea of Japan 41°10′12″ 130°48′ 6″ | 3204 | 12·5 |
| Red clay | Sea of Japan 40°44′48″ 131° 7′48″ | 3261 | 9·5 |
| Red clay | Sea of Japan 39°11′24″ 132°33′48″ | 3046 | 11·2 |
| Mud | Sea of Japan 42° 4′42″ 130°49′14″ | 2304 | 7·0 |
| Blue mud | Sea of Japan 42° 2′ 0″ 130°20′ 0″ | 2796 | 6·2 |
| Blue mud | Sea of Japan 41°11′36″ 130° 4′12″ | 3417 | 12·5 |
| Red clay | Sea of Japan 40°25′12″ 132°45′12″ | 3411 | 9·5 |
| Red clay and blue mud | Sea of Japan 39°36′12″ 133°11′36″ | 1281 | 5·8 |
| Blue mud and sand | Sea of Japan 39°18′ 0″ 133°43′ 0″ | 1261 | 6·2 |
| Blue mud | Sea of Japan 38°48′30″ 133°29′18″ | 1689 | 7·8 |
| Red clay | Pacific Ocean 11°19′ 151°57′ | 5893 | 14·2 |
| Red clay | Pacific Ocean 9°10′ 150°25′ | 5648 | 20·0 |
| | | | Avg. 10·3 |

Since arsenic occurs in igneous quartz, sandstone will always contain some arsenic, in addition to what may be contributed by subsidiary minerals. The number of samples analyzed is too small for significant averaging, but the content is doubtless low in the purer sandstones. An average near 1 p.p.m., possibly between 1 and 2 p.p.m., seems likely.

A sampling of deep-sea sediments, mostly from the Sea of Japan, shows an average of 10 p.p.m. As (Table 15). Only one sample of the fourteen falls outside the limits 5-15 p.p.m. The average of six red clays, two from the Pacific Ocean, is 13 p.p.m.

### C. *Metamorphic rocks*

Table 16 lists arsenic values for the regionally metamorphosed Thomson formation of eastern Minnesota (Schwartz, 1942), and for some miscellaneous samples of

*Table* 16. *Arsenic in metamorphic rocks*

| *Sample* | As, *p.p.m.* |
|---|---|
| *Thomson formation, Minnesota* | |
| Slate, Thomson | 17·6 |
| Slate, Thomson | 9·2 |
| Slate, Carlton | 1·7 |
| Graywacke, near Duluth | 2·3 |
| Graywacke, Atkinson | 9·7 |
| Phyllite, Barnum | 4·0 |
| Phyllite, Barnum | 0·5 |
| Phyllite, Little Elk, Morrison Co. | 0·7 |
| Schist, Denham | 0·7 |
| Quartzose garnet schist, Denham | 0·4 |
| Garnet schist, So. Aitkin Co. | 0·5 |
| Gneiss, near Denham | 0·5 |
| Gneiss, near Denham | 0·8 |
| *Miscellaneous* | |
| Slate (Rove), Gunflint Lake, Minn. | 1·0 |
| Slate (red), iron formation, Cuyuna Range, Minn. | 11·6 |
| Slate (red), Granville, N.Y. | 3·3 |
| Slate, N.Y. | 11·5 |
| Slate, N.Y. | 8·6 |
| Slate, N.Y. | 5·0 |
| Slate, N.Y. | 0·9 |
| Slate (green), Powlet, Vt. | 4·3 |
| Slate, Hidaka, Hokkaido, Japan | 15·7 |
| Quartzite, Dell Rapids, S.D. | 2·2 |
| Basalt hornfels, Duluth, Minn. | 0·7 |
| Amphibolite, Funatsu, Gifu Pref., Japan | 2·2 |
| Green schist, Kune Mine, Shizuoka Pref., Japan | 0·6 |
| Graphite schist, Kune Mine, Shizuoka Pref., Japan | 0·0 |
| Granodiorite gneiss, Funatsu, Gifu Pref., Japan | 1·8 |
| Biotite gneiss, Samani, Hokkaido, Japan | 2·2 |
| Coarse migmatite, Samani, Hokkaido, Japan | 4·1 |

scattered origin. The slate and graywacke of the Thomson series show strongly variable arsenic contents, probably reflecting the variable sulphide and carbonaceous contents, although other factors may be involved. Pyrite isolated from Thomson slate contained 450 p.p.m. As. The phyllites are also variable. The schists and gneisses appear to be more uniform and to have a lower arsenic content (average of five is 0·6 p.p.m. As) than the slates and graywackes. More extensive sampling is required before definite conclusions can be drawn, but apparently arsenic was lost in the end-stages of the regional metamorphism.

The slates among the miscellaneous samples of Table 16 show amounts of arsenic comparable to those in shales.

## IV. Cycle and Balance of Arsenic

Arsenic is probably conveyed to the sea and into sediments to a large extent in association with suspended matter: in detrital minerals, in clay minerals, in adsorbed form on hydrous iron oxides, etc. Doubtless some arsenic is present in solution in ionic or molecular form. The average arsenic content of sea-water is probably less than 0·01 p.p.m.; the total arsenic in the sea is accordingly much less than 1 per cent of that in all sedimentary material.

The preference of arsenic for sediments rich in iron oxides, sulphides, and probably organic matter, is understandable from its general chemical properties.

The much higher content of arsenic in shales as a whole and in deep-sea sediments than in igneous rocks shows that arsenic in sedimentary material cannot have been wholly derived from the weathering of an equivalent quantity of average igneous rock.* This qualitative conclusion is reinforced by the following semi-quantitative considerations.

Opinions differ as to the relative and absolute amounts of continental and deep-sea sediments, and the proportion of shale, sandstone, and limestone in the former. We will first base the calculations on the proportions and amounts obtained by Goldschmidt's geochemical method (Goldschmidt, 1933). According to Goldschmidt, weathered igneous rock amounts to $1{\cdot}6 \times 10^5$ g per cm$^2$ of the earth's surface.† Dispensing with refinements unnecessary for the present purpose, one may say that an equal weight of sedimentary material has resulted, with the proportions 80 per cent shale and clay, 10 per cent sandstone, and 10 per cent limestone and dolomite (Goldschmidt's figures are 91 per cent clastics and 9 per cent limestone and dolomite). The arsenic content of shales and deep-sea sediments (predominantly red clay) will be taken as 10 p.p.m., and that of sandstone and limestone as 1·5 p.p.m. We then have:

$$\text{As from igneous rock} = 1{\cdot}6 \times 10^5 \times 2 \times 10^{-6} = 0{\cdot}32 \text{ g/cm}^2$$

$$\text{As in sediments} = 1{\cdot}6 \times 10^5 (0{\cdot}8 \times 10 + 0{\cdot}2 \times 1{\cdot}5)10^{-6} = 1{\cdot}32 \text{ g/cm}^2$$

* This conclusion would not be valid if (1) the amount of weathered igneous rock was much greater than sedimentary material now in existence, and (2) the weathered material, from which more or less arsenic had been leached, was transformed by ultrametamorphism into "igneous" rocks with distinctly lower arsenic contents than the parent igneous material. Even if (1) is true (cf. Rankama, 1954), (2) probably is not (igneous rocks do not differ greatly in arsenic content), and the available data favour the view that not all arsenic in sediments has been derived from igneous rocks by weathering.

† Wickman (1954) has recently given $1{\cdot}94 \times 10^5$ g/cm$^2$ as the most probable amount of weathered igneous rock as determined by the geochemical method.

The extra arsenic amounts to 1·0 g/cm². The magnitude of this figure is such as to warrant the conclusion that arsenic from the weathering of igneous rocks can not account for all the sedimentary arsenic. Even if shale and clay contain only 5 p.p.m. As, an unlikely value, the excess arsenic would amount to 0·69–0·32 = ~0·4 g/cm². To obtain a balance with 5 p.p.m. As in shale and deep-sea sediments, an average of about 4 p.p.m. As in igneous rocks would be required, or about double the value estimated from the present data.

A second calculation can be made on the assumption that the amount of weathered ingeous rock is approximately double that taken for the preceding calculation. According to Kuenen (1946), all sedimentary material amounts to $7 \times 10^8$ km³, of which continental sediments make up $2 \times 10^8$ km³, the remainder being chiefly oceanic red clay. For simplification justifiable for the present purpose, we will adopt the approximation that continental sediments correspond to $1{\cdot}0 \times 10^5$ g/cm² and deep-sea sediments to $2{\cdot}0 \times 10^5$ g/cm², and the igneous rock from which they are derived to $3{\cdot}0 \times 10^5$ g/cm². Taking Pettijohn's (1949) proportions for sedimentary rock types, slightly rounded to 60 per cent shale, 20 per cent sandstone, and 20 per cent limestone, we find:

$$\text{As from igneous rock} = 3{\cdot}0 \times 10^5 \times 2 \times 10^{-6} = 0{\cdot}6 \text{ g/cm}^2$$

$$\text{As in sediments} = 1{\cdot}0 \times 10^5(0{\cdot}6 \times 10 + 0{\cdot}2 \times 1{\cdot}5 + 0{\cdot}2 \times 1{\cdot}5)10^{-6} + 2 \times 10^5 \times 10 \times 10^{-6} = 2{\cdot}66 \text{ g/cm}^2.$$

The extra arsenic amounts to ~2 g per cm². The relative amounts of arsenic in igneous rock and sediments remain practically the same as in the first method of calculation, as is to be expected.

If the assumption is made that the weathered igneous rocks supplying the sediments had much the same arsenic content as the igneous rocks now accessible, the excess arsenic must have been derived from volcanic exhalations and hot springs, possibly with a greater or less contribution from some atmosphere or ocean of pre-geologic time. That arsenic is today being transported to the surface from deep sources, probably ultimately magmatic, appears likely from the appreciable arsenic content of many thermal waters (see, for example, the compilation in Gmelin, 1952, p. 32). The hot springs of Yellowstone Park contain as much as 2 or 3 mg As per litre (Fig. 3) together with boron and much chloride. Because of the low arsenic content of igeous rocks it seems impossible that the appreciable arsenic content of many hot-spring waters from igneous areas can generally result from rock leaching. Arsenic is also known to be a not uncommon, though minor, constituent of volcanic sublimates and incrustations.

It is of interest to compare the escaping tendency of arsenic with that of some other elements. Relative values can be obtained by dividing the excess of element (in sediments, ocean, and atmosphere), expressed in g/cm², by its average concentration in igneous rocks. It is somewhat more satisfactory to replace the concentration in igneous rocks by the amount of element (g) in the frustum of a cone with a 1-cm² base at the earth's surface, and extending downward 60 km through the granitic and basaltic shell. An idea of the absolute escaping tendency is thus obtained, even though the basis is necessarily arbitrary. Escape ratios for a

number of elements defined in this way have been reported (KURODA and SANDELL, 1953). Some of these are given below for comparison with arsenic:*

| | | | | | |
|---|---|---|---|---|---|
| As | 0·03 | B | 0·5 | S | 0·05 |
| $H(H_2O)$ | 1·2 | C | 0·4 | Cu | ~0·002 |
| Cl | 2·0 | N | 1 | Zn | ~0·002 |

For elements such as arsenic which are contained largely or entirely in sedimentary material, the value of the escape ratio will of course depend on the assumed

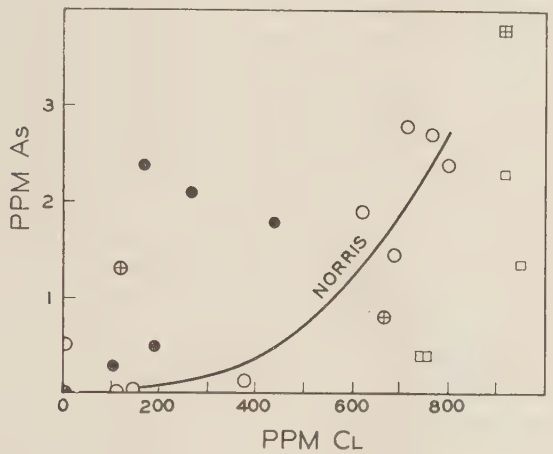


Fig. 3. Arsenic content of volcanic spring waters as a function of the chloride content.
○ Norris Basin, Yellowstone Park, ALLEN and DAY (1935).
⊕ Norris Basin, Yellowstone Park, GOOCH and WHITFIELD (1888).
● Other Yellowstone springs.
□ Steamboat Springs, Nev., BRANNOCK *et al.* (1948) and WHITE and BRANNOCK (1950).
⊞ Steamboat Springs, Nev., ALLEN and DAY (1935).

quantity of sediments. The above values are based on GOLDSCHMIDT'S figure of about $1{\cdot}6 \times 10^5$ g of sedimentary material per square centimetre of the earth's surface. Probably a figure twice as great for sedimentary material is a better estimate (KUENEN, 1949), and the escape ratio for arsenic then becomes double the value tabulated above, or 0·06. On the same basis the escape ratio for sulphur will be increased to about 0·07 (the increase is not twofold, because much of the exhaled sulphur is present in sea-water). The values for $H_2O$ and Cl remain unchanged; that for C should be increased, probably to about 1. Perhaps the ratio for B should be larger, but the present data are uncertain. Obviously the escape ratios calculated are at best only rough approximations, but the magnitudes are significant.

* The calculation for arsenic may be given as an example. The amount of arsenic that has escaped is about 1·0 g/cm². The mass of material from which this is assumed to be derived is $6 \times 10^6 \times 3 \times 1 = 1{\cdot}8 \times 10^7$ g/cm² (3 = average density). The amount of arsenic in this mass is $2 \times 10^{-6} \times 1{\cdot}8 \times 10^7 = 36$ g/cm², if the average arsenic content is taken as 2 p.p.m. Therefore, the escape ratio is 1·0/36 = 0·03.

Arsenic occupies an intermediate position between such elements as $H(H_2O)$ and Cl, which are highly atmophilic and hydrophilic, and Cu and Zn (and most other metals), which are very slightly so. Arsenic closely resembles sulphur in its escaping tendency. An appreciable mobility of arsenic is to be expected from the physical and chemical properties of some of its compounds. $AsCl_3$, $AsF_3$, and $As_2O_3$ are volatile at relatively low temperatures; $As_2O_3$ is water-soluble, and arsenic sulphides dissolve readily in alkaline sulphide solutions (formation of thioarsenites and thiorsenates) or in alkaline solutions alone.

That the escaping tendency of arsenic should be less than of chlorine is in harmony with the stronger lithophilic character of the former. In the crystallization of a magma, arsenic enters the lattices of silicate and oxide minerals by replacing silicon, aluminium, iron, and possibly other elements, as already shown. On the other hand, chlorine shows little tendency toward isomorphous replacement, except of $OH^-$ or $O^=$. As crystallization proceeds, the ratio Cl/As increases in the liquid fraction. In general it may be expected that the greatest loss of volatiles will occur in the later stages of the crystallization of a magma mass. Accordingly it seems reasonable to expect that a greater fraction of total chlorine than of total arsenic will escape. Even if the volatility of arsenic were greater than that of chlorine in the end stages, the relative loss of chlorine could well be greater for the whole process. The average ratio As/Cl in igneous rocks is not far from 0·01 (2 p.p.m./200 p.p.m.), as contrasted with 0·0004 for the volatiles, assuming that the excess of the elements in the sea and in sediments ($\sim 3 \times 10^5$ g/cm$^2$) represents their amounts in the magmatic emanations.

Urey (1953), basing his conclusion on the older abundance values for arsenic in igneous rocks and sediments, has pointed out that As/Cl in the hot springs of Yellowstone Park and in Steamboat Springs, Nevada (0·005, 0·002), is much higher than in the ocean and sediments. This apparent discrepancy, although reduced, remains with the use of the new abundance data, as the value given in the preceding paragraph shows. However, we do not know how well these waters represent the average magmatic contribution. Since the escaping tendencies of elements are not equal, the ratio of two elements in the volatile fraction will not, in general, remain constant, but will vary with time. Under constant conditions, the ratio of the more volatile to the less volatile element should decrease with time. The existence of fractionation of this kind was proposed long ago by St. Claire-Deville to explain the variation of volatile constituents at different stages of volcanic activity. The actual course of fractionation must be very complex, since the escaping powers of the volatile constituents will vary differentially with temperature, composition of the magma, and many other factors, including the effect of the preponderant volatile elements on the minor elements.

Because chloride is an abundant constituent of fluids from magmas, and $AsCl_3$ is easily volatile, some relation between the amounts of chlorine and arsenic in thermal waters from presumably magmatic sources might exist. Therefore, a plot has been made of As versus Cl in the hot springs of Yellowstone Park and in Steamboat Springs, Nevada (Fig. 3), for which a fair number of arsenic determinations are available. For comparison with a constituent which should not be

directly influenced by chlorine, boron has also been plotted against chlorine for the Yellowstone springs (Fig. 5).

If arsenic escapes from magmas or their environs predominantly as $AsCl_3$, its concentration in magmatic waters might increase faster than the chloride content, in consequence of the reaction

$$As_2O_3 + 6HCl \rightleftharpoons 2AsCl_3 + 3H_2O,$$

assuming the existence of loci at which the concentration of HCl may vary as the result of different concentrations of $Cl^-$, $H_2O$, varying temperature, etc. Hydrogen chloride is assumed to form by hydrolysis of chloride. Arsenious chloride possibly could be formed in other ways, as represented by the schematic reaction

$$As_2O_3 + 6NaCl + 3SiO_2 \rightleftharpoons 2AsCl_3 + 3Na_2SiO_3,$$

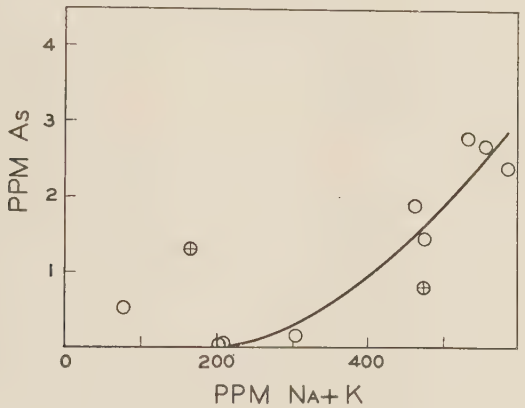


Fig. 4. Arsenic content of Norris Basin hot springs, Yellowstone Park, as a function of Na + K content.

○ Allen and Day (1935).

⊕ Gooch and Whitfield (1888).

without altering the argument. On the other hand, arsenic might be volatilized, largely as $As_2O_3$, especially with water vapour, and there would then be only an indirect relation between volatilized arsenic and other volatile elements. The liberated chlorine should eventually find its way to the surface without being retained by precipitation, but arsenic might well be precipitated en route. Also in the ground-water zone, reactions may occur leading to precipitation of such elements as arsenic. Thus the interpretation of surface-water analyses is subject to uncertainties.

No close relationship exists between As and Cl in the Yellowstone springs as a whole (Fig. 3).* However, for the springs of the Norris Basin (mixed type, chloride and sulphate waters, with and without bicarbonate), there is an indication

* In five thermal waters of Umnack Island (Aleutians) analyzed by Byers and Brannock (1949), no simple relation between As and Cl (or between As and B) is evident. Arsenic values for New Zealand hot springs are scanty. Wilson (1949) reports arsenic contents of 0·4 and 6·0 p.p.m. for two springs of this region.

that arsenic tends to approach zero before chlorine does.* Also, if arsenic is plotted against Na+K, As is found to decrease to zero at about 200 p.p.m. Na+K (Fig. 4). Evidently the variation of As with Cl or Na+K is not due solely to dilution of magmatic water by ground water. Further than this, the matter is speculative. The content of Cl or Na+K in the waters is doubtless a measure of volatile magmatic products. Some indication is given that arsenic rises exponentially with chlorine in waters of the same area, but the data are too scanty for a certain conclusion. This behaviour may be the result of the mass-action effect of chlorine at or near

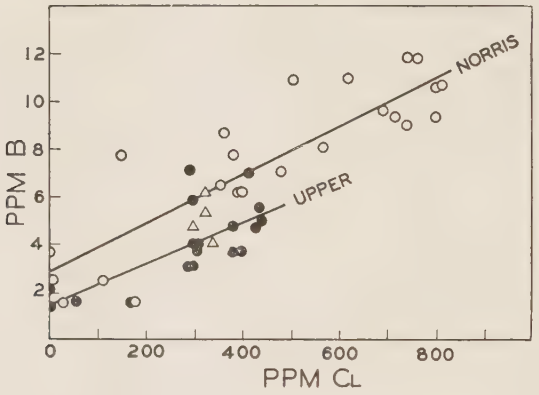


Fig. 5. Boron content of Yellowstone Park hot-spring waters as a function of the chloride content. Data from Allen and Day (1935). Lines drawn by least squares.

○ Norris Basin.
● Upper Geyser Basin
△ Lower Geyser Basin.

the magma source as postulated above. An alternative explanation is that on dilution the juvenile water deposits arsenic underground, the deposition being almost complete before the dilution by ground water is extensive. Although arsenic sulphides and scorodite (ferric arsenate) are found in some of the spring deposits, precipitation apparently takes place to only a minor extent at or near the surface.

Evidence is fairly convincing that boron does not decrease to zero with chlorine in the Yellowstone waters (Fig. 5). The explanation seems to be that although chlorine is an index element for volatile elements, including boron, it does not play a direct role in the escape of this element, which, as boric acid, is volatile with steam.

The ratio $\Sigma As/\Sigma B$ for fourteen Yellowstone springs is 0·16 and for four Steamboat Spring waters 0·02 (Brannock *et al.*, 1948). The calculated value of As/B

* The aberrant point at 5 p.p.m. Cl and 0·5 p.p.m. As (Spring No. 33) represents an acid water containing 1105 p.p.m. $SO_4$ and 342 p.p.m. $NH_4$, and is thus distinctly different from the other Norris waters for which Allen and Day reported arsenic contents. Such acid waters are believed (White and Brannock, 1950) to result when steam carrying hydrogen sulphide, but not hydrogen chloride, is condensed at or near the surface; sulphuric acid is formed by air-oxidation of hydrogen sulphide. The reason for the presence of appreciable arsenic is obscure. There is no reason to believe that arsenic should be transported with hydrogen sulphide in the vapour phase. Possibly because of its acid character, this water has leached arsenic from surrounding material.

*Table* 17. *Arsenic in meteorites*

| | As, *p.p.m.* |
|---|---|
| *Irons* | |
| Canyon Diablo | 8·0, 8·2 |
| Henbury | 3·2, 3·9 |
| *Chondrites* | |
| Alamogordo, N. Mex. | 2·9 |
| Arriba, Colo. | 3·5 |
| Beenham, N. Mex. | 0·8 |
| Cope, Colo. | 4·0 |
| Cotesfield, Neb. | 2·3 |
| Estacado, Texas | 2·6 |
| Silicate phase | 0·0 |
| Gladstone, N. Mex. | 2·8 |
| Silicate phase | 0·3 |
| Gruver, Texas | 2·6 |
| Kingfisher, Okla. | 1·8 |
| Ladder Creek, Kans. | 0·9 |
| Melrose, N. Mex. | 2·1 |
| Morland, Kans. | 1·7 |
| Silicate phase | 0·6 |
| Plainview, Texas | 0·9 |
| Silicate phase | 0·0 |
| Metal phase | 11 |
| Roy, N. Mex. | 2·1 |
| Avg. of chondrites | 2·2* |
| Composite I (Arriba, Beenham, Cope, Cotesfield, Morland, Plainview, Roy) | |
| Silicate phase | 0·4 |
| Metal phase† | 11 |
| Sulphide phase | 8‡ |
| Composite II (Alamogordo, Estacado, Gladstone, Gruver, Kingfisher, Ladder Creek, Melrose) | |
| Silicate phase | 0·2 |
| Metal phase† | 13 |
| Sulphide phase | 11§ |
| *Tektite* | |
| Muldoon, Texas | 0·6 |

* Analysis of composite gave 2·3 p.p.m. As.
† Correction applied for silicate in metal fraction.
‡ ±50 per cent.
§ ±30 per cent.

for sediments, assuming an average B content of 150 p.p.m., is 0·05, a value subject to great uncertainty however.

## V. Arsenic in Meteorites

Table 17 contains the meteorite data. The average for fourteen chondrites is 2·2 p.p.m. As, with a range from 0·8 to 4·0 p.p.m. The average of the metal phase of these chondrites is 12 p.p.m. As (the mean of two composites having 11 and 13 p.p.m.). The troilite of the same chondrites contain an average of ~10 p.p.m. As. This figure is very approximate, because the small amount of sample may lead to an error of 30-50 per cent. The average for the silicate phase of the chondrites is 0·3 p.p.m. (the mean of 0·2 and 0·4 p.p.m. averages for two composites). This value is to be looked upon as somewhat approximate, because, in order to remove troilite, the silicate was leached with cold, dilute acid, and some arsenic may have been dissolved in the process. Error due to possible unremoved sulphide is less likely. Indirect evidence points to an upper limit of about 1 p.p.m. As in the silicate phase, because more than this would result in a figure greater than ~2 p.p.m. for the sum of all the phases.

The above values show that the siderophilic and chalcophilic characters of arsenic are strong, and much the same quantitatively. The arsenic content of the silicate phase of chondrites appears to be less than that of ultramafic rocks (the latter ~1 p.p.m.).

Our average for chondrites is much less than the average of 18 p.p.m. As reported by the Noddacks (1934). If, following Urey (1952), we take chondrites to represent average cosmic matter (excluding gaseous and volatile elements), we obtain the cosmic atomic ratio $As/Si = 5 \times 10^{-6}$, assuming no undue loss of arsenic by volatilization. Arsenic (atomic number 33) is less abundant, than germanium (A.N. 32) and selenium (A.N. 34) if the respective contents are taken as 2·2, 70, and 7 p.p.m. in chondrites.

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# Contribution of metallurgy to the origin of meteorites

## Part II—The significance of Neumann bands in meteorites

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ABSTRACT

Neumann bands in alpha iron are produced by shock waves, their formation occurring readily at low temperatures but not at all at high temperatures. They represent lamellae of mechanically twinned metal, where twinning of the crystal along the (112) planes more easily accommodates sudden shear than does slip. Reinforcement and interference of reflected shock waves probably account for the serrated outline and frequent convolution of the bands.

The bands make up characteristic metallographic markings of hexahedrites and of kamacite in octahedrites. They reveal, therefore, that sometime in history after the Widmanstätten pattern formed (in the case of octahedrites) and at relatively low temperatures, meteorite bodies were subjected to violent impact or explosion. The appearance of acicular phase transformation products both within and without Neumann bands of the Dexter meteorite constitute evidence that the bands were formed previous to collision with the earth. It is proposed that the shock wave to which the parent body was subjected first formed Neumann bands, followed by pressure changes which produced observed transformation products throughout kamacite, including twinned metal. The necessary conditions for transformation include a temporary increase of pressure brought about perhaps by distortion or impact, followed by sudden release of pressure, such as would accompany fragmentation of a large body.

### Nature of Neumann Bands

Neumann, a little over 100 years ago, observed markings in meteorite structures appearing to the unaided eye as a multitude of straight lines, and under the microscope as narrow bands. They are now known as Neumann bands or Neumann lamellae. In three dimensions they are lenticular in shape, appearing, therefore, as lines or bands when viewed in cross section. The lamellae can be produced in iron artificially by subjecting the metal to shock or impact. This explains their presence, for example, in sections of old suits of armour where the protective cladding was once worn by an aggressive knight who dealt hard blows with his spear or axe and received some in return.

Neumann bands, in fact, can form in body-centred cubic iron at room temperature only when the lattice is suddenly distorted by external stress. Should instead the deformation proceed slowly, slip occurs along certain crystallographic directions of the lattice, resulting in planes of atoms being displaced with respect to neighbouring planes. These planes make up slip bands, and the iron is said to deform plastically. The action is not unlike a deck of cards moving over each other (Fig. 1). But under sudden impact or shock, where deformation must proceed more rapidly, twinning is the mechanism of plastic deformation. This is illustrated in Fig. 2. Atoms of region $ABCD$ move suddenly into position as here shown, becoming the mirror image of the metal atom arrangement on the other side. Shear by this mechanism occurs inherently more rapidly than can occur by slip.

Crystallographically, Neumann bands are twinned metal in the alpha or body-centred cubic lattice of iron and iron alloys. Because they are produced by mechanical forces, they are called mechanical twins. This distinguishes them from annealing twins where the source of twinning is recrystallization of the metal by heat

treatment. Mechanical twins do not form as readily in gamma or face-centred cubic iron alloys (taenite of meteorites), presumably because the face-centred cubic lattice deforms relatively easily by slip along the (111) planes even at high rates of deformation. By comparison, there is no analogous preferred slip plane in the body-centred cubic lattice, and the actual slip planes entering deformation are more complex.

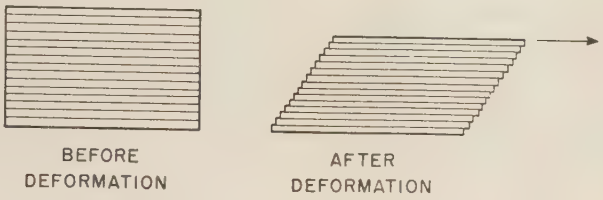


Fig. 1. Plastic deformation along slip planes.

Defining Neumann bands as mechanically twinned metal has been under discussion since the early days of metallurgy, some investigators contending that the bands instead may be cold-worked or disorganized metal. Arguments for the latter point of view have been summarized most recently by Zapffe (1946). However, the bulk of evidence is in favour of twinning as shown by etch pit orientation studies within and without the bands (Harnecker and Rassow, 1924;

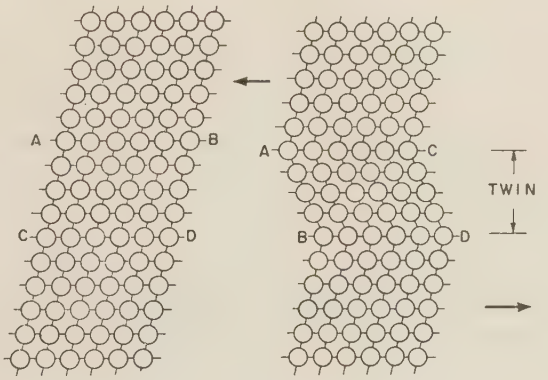


Fig. 2. Plastic deformation by twinning.

Smith, Dee, and Young, 1928); X-ray studies (Mathewson and Edmunds, 1928), hardness tests (Bruckner, 1951; Dalton, 1950), as illustrated by Fig. 3*; by measuring the angle between the twinning direction and the angle of shear (Paxton, 1953); and by differing rates of etching depending on differing orientation within and without the bands, as shown by photomicrographs (Foley and Howell, 1923) and surface replica studies described below.

Mechanical twinning is favoured as a mode of shear as the temperature is

* If the hardness indentation includes the interface between Neumann band and matrix, higher readings are sometimes found because of variable amounts of cold worked metal in this region. Elsewhere hardness is the same within or without the bands.

lowered. At liquid air temperatures, for example, relatively slow deformation is sufficient to produce Neumann bands in pure iron, compared with the severe shock such as impact with a bullet required at room temperatures. Above room temperatures, the shock must be of greater magnitude, and at sufficiently high temperatures, bands do not form at all. A few per cent silicon alloyed with iron favours formation of Neumann bands, which explains the fact that bands in commercial silicon steel form by comparatively slow deformation at room temperature.* Also, presence of phosphorus aids formation of bands, a significant fact in view of the usual presence of phosphorus in meteorites. Robin (1910, 1911) found that Neumann bands could be produced in a steel containing 1 per cent phosphorus at as high a temperature as 600°C, but not at 700°C. In single crystals of iron, the minimum temperature is much lower (Pfeil, 1926).

## Effect of Compressional Waves

Evidence has accumulated, some of which is described for the first time herewith, suggesting that the shear forces producing Neumann bands are the result of a compressional wave entering the metal from the local point of impact and which travels through the metal at a velocity of about 5000 metres/sec. The directed moving front of temporarily displaced atoms shears the crystal along lattice planes where shear most readily takes place, causing twinning.

The preferred crystallographic planes for twinning of alpha-iron are the trapezohedral (112) planes. These planes make up sides of the 24-face figure called the icositetrahedron or trapezohedron; hence, Neumann bands can follow a maximum of perhaps twelve different directions in a single crystal. But because the initial compressional wave is usually directional, it is uncommon to find bands oriented along all of the possible directions. Also, since the initial wave is reflected or scattered in a variety of directions partly by grain boundaries or phase discontinuities, and partly by the geometric boundaries of the specimen itself, it is also probable that at areas where reflected waves reinforce each other additional shear occurs. This can account for a second Neumann band crossing a first band a moment after the first has formed (Fig. 4) and may also suggest why bands sometimes have serrated edges and segmented shapes (Figs. 3, 4, 5).

In accord with this picture, Neumann bands pinch off at grain boundaries or at phase discontinuities where shear is constrained. In addition, Neumann bands in meteorities either terminate at taenite areas, or the shear forces are transmitted along slip planes.† A band once formed acts like a grain boundary or phase discontinuity serving often to limit but not necessarily stop shear across it by a subsequent wave at an angle to the first. When a second band crosses a first band, the first is displaced a distance equal to the actual shear produced in forming the second (Fig. 4).

The characteristic convolutions of Neumann bands as influenced by complex shock waves can be illustrated by lightly tapping an asbestos composition board on

* Silicon in meteorites occurs mostly as silicate inclusions. These would not aid Neumann band formation as does alloyed silicon and might, if sufficiently numerous, make conditions less favourable for mechanical twinning.

† An excellent example is included in Plate 76–1 (Perry, 1944).

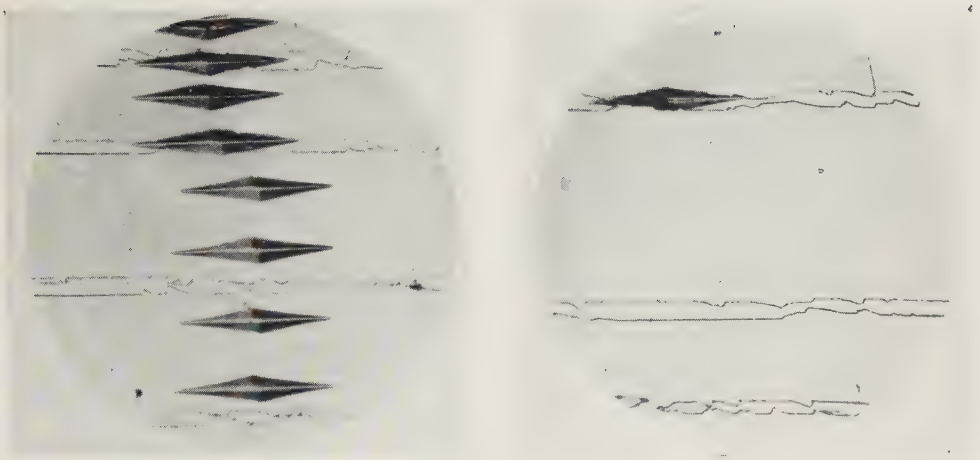

Fig. 3. Hardness measurements of Neumann bands in hydrogen annealed 3/16-inch electrolytic iron rod. Bands formed by impact with 0·22 calibre bullet. Average Knoop hardness within bands —91, in matrix —95. (These values are the same within experimental error.) × 500 (reduced to $\frac{7}{10}$).

Fig. 4. Neumann bands in electrolytic iron produced by 0·22 calibre bullet. The vertica band formed first, was then displaced twice by the shear accompanying formation of two horizontal bands. × 500 (reduced to $\frac{5}{10}$).

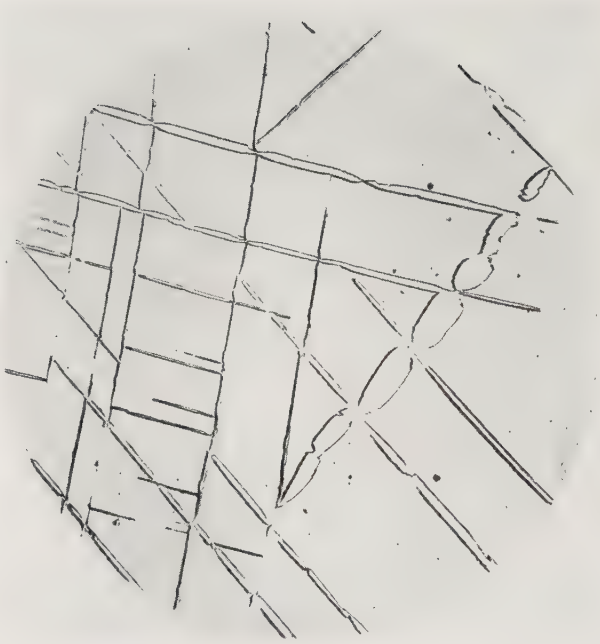

Fig. 5. Intersecting Neumann bands in electrolytic iron produced by 0·22 calibre bullet. Broad segmented band is oriented at a small angle to the plane of the surface. × 250 (reduced to $\frac{8}{10}$).

Before vibration.

After vibration.

**Fig. 6.** Illustration of Neumann band shapes by patterns of lycopodium powder on a vibrating board. $\times$ 2 (reduced $\frac{8}{10}$).

Fig. 7. Neumann bands in mild steel produced by hammer blow at liquid air temperature showing preferred formation in large grained ferrite. Upper region decarburized; lower region contains pearlite (dark) and ferrite. × 500 (reduced to $\frac{8}{10}$).

Fig. 8. Neumann bands in electrolytic iron produced by 0·22 calibre bullet. The 3/16-inch rod, bent by impact, shows corresponding curvature of Neumann bands in region of maximum distortion.

which linear ridges of lycopodium powder are placed, as shown in Fig. 6. Vibration of the board sets up two-dimensional waves which in certain areas reinforce or interfere with each other. These areas, often in elliptical in shape, are outlined by the powder. As with Neumann bands, the ellipses are usually not all the same size or shape. The analogy is not perfect, but effect of vibration on the powder is similar in some respects to the causes of peculiar shapes assumed by twinned volumes of the iron lattice stressed by a complex variety of primary and secondary high-amplitude compressional waves.

The fact that low temperatures or additions of silicon or phosphorus to iron favour Neumann band formation can be explained not only by increased difficulty of slip under these conditions but, perhaps, in addition, by the circumstance that any sudden slip in the metal, induced by stress above the critical value for plastic flow, sets up a shock wave having the same effect as impact, and resulting in mechanical twinning of adjacent portions of the crystal. A similar suggestion has been offered for Neumann band formation in silicon iron (Tipper and Sullivan, 1951) stressed to the point of fracture.

A fine grained iron or one containing carbide areas, such as a commercial steel, is less favourable to Neumann band formation because the various phase discontinuities attenuate the shock wave, and also the small dimensions of the crystal decrease possibility of shear. This is shown in Fig. 7 for a carbon steel rod decarburized (carbon removed) in part at the surface by heating in hydrogen at high temperatures. The decarburized steel rod was cooled to liquid air temperatures and then struck a hammer blow, thereby producing numerous bands in the low carbon area where ferrite grain size is large, but only an occasional band in the conglomerate of pearlite (a mixture of lamellar cementite and ferrite) and alpha-iron (ferrite).

Evidence that Neumann bands are formed by the initial shock waves before slower deformation or bending of the metal along slip planes is shown by Fig. 8. A rod of electrolytic iron about 2 inches long and 3/16-inch in diameter was hit by a 0·22 calibre (long) bullet at room temperature and was partly fractured by the impact. Metallographic examination of the fractured area shows curved Neumann bands which were presumably straight when first formed, since they are produced along the (112) planes. Therefore, the logical conclusion is that they formed first by the shock wave at the time the bullet struck and were then bent as the bullet continued its path through the specimen.

## Identifying Twinned Metal by Etching

Twinned metal constituting a Neumann band is differently oriented with respect to background metal, and corrodes, therefore, at different rates in etching reagents. For this reason, boundaries between the twinned and parent metal are revealed by metallographic etching for the same reason that differently oriented grains of a metal are made visible by differing rates of chemical attack. Slip bands, on the other hand, are usually not visible after etching because the orientation of metal is not disturbed. However, they may become visible when precipitates are formed along the slip planes. Berwerth and Tammann (1912) thought that Neumann bands represented strained or cold-worked metal, and, hence, were visible because

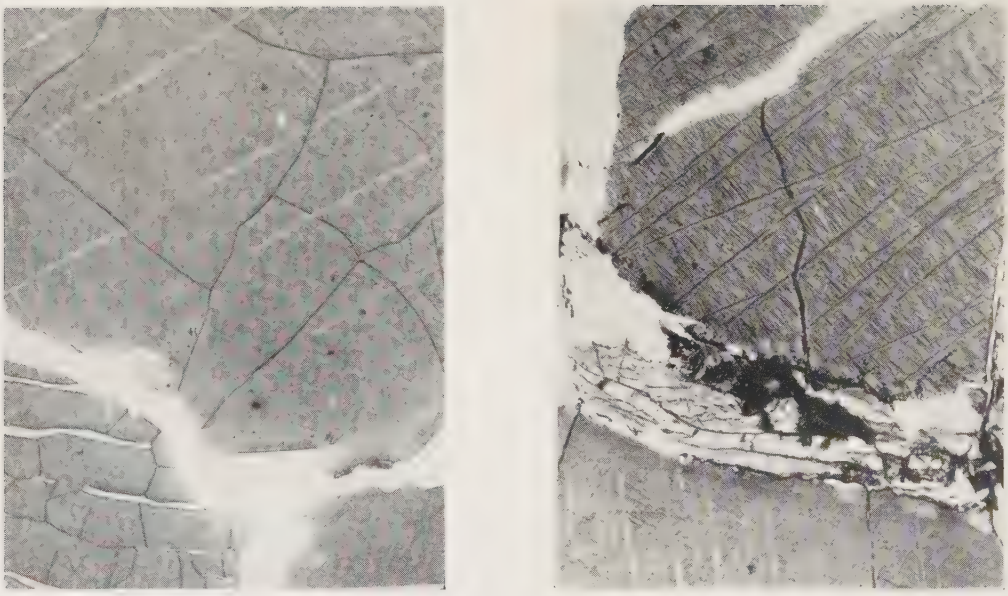

Fig. 11. Parlodian replicas of Dexter meteorite (7·9 per cent Ni) showing light and dark Neumann bands. Variation of shading within lamellae of left figure reveal transformation product. × 100 (reduced to $\frac{7}{10}$).

they also are not observed in plastically deformed ferrite (PFEIL, 1926). There is correspondingly no report of their formation in martensite, and it is doubtful that mechanical twinning could easily occur under any conditions in a phase broken up by shear or by precipitation along multitudinous planes of the crystal.* The currently available evidence, therefore, does not suggest that Neumann bands formed within the observed transformation product, and since bands do not form in taenite, the significant conclusion is that they probably formed first in clear kamacite after which the acicular transformation took place throughout the kamacite phase. There is no indication how far apart in time these two supposed events took place, although the cited order of their occurrence is plausible.

It is probable and well within reason that the shock wave accounting for the Neumann bands was attended by high compression (e.g., shifting gravitational fields or distortion) of sufficient duration to transfer the alloy temporarily from the $\alpha$ region of the phase diagram to the $\alpha$ plus $\gamma$ or even $\gamma$ region of the high-pressure diagram at the same or slightly higher temperature (Fig. 8, Part I). A temperature rise of alloy already under pressure followed by release of pressure could accomplish the same thing. Acicular kamacite in both matrix and in Neumann bands may then have originated in one of two ways:

(1) Taenite ($\gamma$) precipitated out of the corresponding supersaturated kamacite ($\alpha$) forming the observed acicular structure.

(2) The alloy transformed wholly or in part to $\gamma$ phase, which phase then transformed to acicular $\alpha_2$ phase upon resumption of lower pressures.

In absence of further information, greater weight should probably be placed on transformation (1) above, because transformation of $\alpha$ to $\gamma$ phase, under laboratory conditions at least, would be expected to erase the Neumann bands, whereas this would not apply to precipitation of $\gamma$ from $\alpha$.† X-ray orientation studies may be able to distinguish between the two transformations, but such measurements have not yet been undertaken.

The observed Neumann bands could have formed only at relatively low temperatures, presumably below 300°C and definitely not above 600°C, because Neumann bands do not form above the latter temperature.‡ Furthermore, any supposed temperature rise following the shock wave could not have persisted for long periods if it reached as high as 400°C; otherwise, the transformation product and Neumann bands would have been erased. The bands in Mount Joy meteorite were found to disappear after a few minutes of heat treatment at about 900°C (BERWERTH and TAMMANN, 1912); the necessary time to do so would be correspondingly longer at lower temperatures.

The pressure transformation of kamacite to taenite according to (2) above is not instantaneous even though, by comparison, the reverse transformation of taenite

* L. KAUFMAN (Special Problem Report to the Dept. of Metallurgy, M.I.T., 1954) has since reported, based on photographic evidence, that he obtained Neumann bands in acicular ferrite of a 5 per cent Ni-Fe alloy by striking a small specimen with hammer at liquid $N_2$ temperature. If this is confirmed, the present thesis of their origin in interplanetary space is less certain, since the observed Neumann bands of Dexter may then also have originated through collision with the earth. However, the metallographic structure observed by KAUFMAN may consist of so-called kinks and not mechanical twins, in which case they have no bearing on the present discussion. The subject obviously requires further study.

† MORRIS COHEN, private communication.

‡ High pressures may possibly shift this critical upper temperature.

to $\alpha_2$ phase is practically so. Bunshah and Mehl report (1953) that the needles of $\alpha_2$ phase in a 29 per cent Ni-Fe alloy form at a rate of 1000 metres/sec, which is somewhat lower than the velocity of sound in the alloy. The martensite-like transformation is diffusionless, being described as a two-stage shear displacement of the face-centred cubic atoms into new positions of the body-centred cubic arrangement. Rate of formation is not greatly sensitive, if at all, to temperature. Transformation of $\alpha$ body-centred (kamacite) to $\gamma$ face-centred (taenite) cubic lattice, on the other hand, requires nucleation and diffusion of the component atoms.* Hence, the rate of $\gamma$ phase formation from $\alpha$ proceeds more rapidly as the temperature is raised for any given pressure sufficient to induce the transformation. At room temperature, it is questionable that the transformation can occur at all within allowable time periods regardless of pressure. Similarly, the precipitation of taenite ($\gamma$) from super-saturated kamacite ($\alpha$) requires time for nucleation and diffusion, although little is known about the actual times required. It would not in any case have reasonable chance of proceeding at room temperatures.

Accordingly, a meteorite colliding with the earth's atmosphere and remaining at ordinary temperatures, as all meteorites do except for an incandescent outer surface, would not bring about a pressure transformation of the kind observed in Dexter regardless of how intense the collision might be. The time is much too short for appreciable transformation of $\alpha$ to $\gamma$ phase. The transformed Neumann bands of the Dexter meteorite, therefore, constitute evidence that *they were formed previous to the time the meteorite entered the earth's atmosphere.* Their presence suggests a shock wave and temporary conditions of increased pressure or temperature or both. This was followed by release of pressure, all of which came below the temperature at which Neumann bands are erased within the time the higher temperature was maintained. If Berwerth and Tammann's data are typical, the maximum was certainly less than 900°C and probably less than 600°C, considering the long time necessary to cool large bodies. Several meteorites exhibit a transformed or acicular kamacite structure†, presumably because these conditions of formation were not uncommon. Since prolonged heat treatment of acicular kamacite in the alpha-phase region converts it to clear kamacite again, there is also the possibility that transformed kamacite may have survived only in those meteorite specimens that cooled relatively rapidly after the pressure transformation. Any heat treatment sufficient to erase the transformation product, however, would also erase the Neumann bands formed previous to transformation.

In summary, metallographic evidence supports the view that:

1. The Widmanstätten pattern of octahedrites formed under conditions of high pressure.

2. Octahedrite structures were formed by very slow cooling from an elevated

* Laboratory experiments show that the $\alpha_2$ phase on heating may transform rapidly to $\gamma$ phase by a shear process, but this is not true of the equilibrium $\alpha$ phase formed on slow cooling of the alloy.

† See Perry (1944), "Primitiva," Plates 10-3, 4; "Trenton," Plates 35–1, 2; "Thunda," Plate 35–3; "Canton," Plate 35-4; "Smiths Mountain," Plate 36–1; "Kenton County," Plates 36-3, 4; "Seneca Township," Plates 73-1, 2; "San Francisco del Mezquital," Plate 78–2. Perry suggests that transformed Neumann bands, as in "Trenton," are really not Neumann bands but $\gamma$-$\alpha$ transformation structures. Yet allowing for some blurring caused by mild heat treatment after the transformation, there is unmistakable identity of the observed structures with bands artificially produced, or with those in other meteorites such as Xiquipilco.

temperature to temperatures in the neighbourhood of 300°C or below. The upper limit of temperature cannot be established precisely, since the higher the pressures during the time of formation, the lower is the minimum temperature necessary to account for the patterns. Formation of Widmanstätten patterns at ordinary or sub-zero temperatures is not possible within times ascribed to the age of the solar system.

3. Absence of the Widmanstätten pattern in meteorites containing more than 12–13 per cent nickel suggests that these alloys remained for the majority of their extra-terrestrial existence as gamma phase under high pressure. Subsequent transformation of gamma (taenite), if it occurred, was relatively rapid through sudden release of pressure or rapid cooling of small bodies. Lack of transformation in ataxites of more than 27 per cent nickel confirms that passage through the transformation temperature was relatively rapid.

4. Plessite phase was formed in part by rapid transformation of taenite to metastable $\alpha_2$ phase through sudden release of pressure. This occurred after the time the Widmanstätten pattern was formed and after the meteorite body had reached low temperatures. Fine and coarse plessite resulted from varying thermal treatment of metastable $\alpha_2$ alloy. Other plessite areas obviously formed by slow cooling of the lower nickel composition areas of inhomogeneous taenite, sometimes forming vestigial Widmanstätten patterns.

5. Acicular kamacite is also proof that drastic pressure changes occurred sometime in the history of meteorites.

6. Neumann bands are evidence that meteorites were subjected to high energy shock waves after the Widmanstätten pattern formed and, hence, after the metallic body or bodies cooled down.

7. Transformation products within Neumann bands in some specimens are evidence that the bands formed before such time that the alloy collided with the earth, and, hence, the shock wave producing them must have occurred in interplanetary or interstellar space. This shock wave may have caused or paralleled fragmentation of a larger body, the smaller gravitational fields at the centre of the fragments corresponding to a sudden pressure release.

## Acknowledgment

Appreciation is expressed to Mrs. Constance Craven for preparing several of the photomicrographs, and to John F. Troughton for assistance in preparing Fig. 11.

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# The spectral-transmissive properties of some of the tektites

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ABSTRACT

Data are given on the spectral ultraviolet, visible, and infrared transmittances of australites, bediasites, rizalites, moldavites, and Georgia tektites, and of Libyan desert glass in relation to that of fused silica and a number of commercial glasses having a high iron or high silica content. Their absorption characteristics, resulting from the incorporated iron oxides, carbon dioxide, and water, offer an opportunity for additional investigations relating to exact temperature, atmospheric, and other conditions connected with their formation and history. The Libyan desert glass in having excessive absorption at 2800 millimicrons does not seem to fit into the general scheme with the true tektites.

## 1. Introduction

Tektites, or glass objects reported as having extra-terrestrial origin, have long been a problem of considerable interest to cosmologists, geologists, astronomers, and to scientists in other related fields. These glasses did not seem to fit in properly with the compositions and structures found in meteorites or with any of the generally accepted theories relating to the origin of the planetary system. In fact it was long considered improbable that they could be of extra-terrestrial origin (Barnes, 1940). On the other hand, their special compositions being that of high-silica glasses having as major secondary constituents the oxides of aluminium, iron, magnesium, calcium, sodium, and potassium, did not compare with that of any of the igneous rocks or other volcanic materials. In this respect they differ markedly from obsidian. The compositions of tektites actually are more closely matched, however, by certain sedimentary rocks, hence many investigators have tried to connect their origin with some process whereby terrestrial sedimentary material may have been sufficiently heated to form glass. However, since these glasses have melting-points ranging several hundred degrees above that of ordinary industrial glass, it has been generally agreed that no natural heat-source has existed upon this earth within recent geologic time capable of producing temperatures adequate for this purpose.

The study of the tektite glasses is therefore another avenue of approach to a fuller understanding of some of the cosmological problems connected with the formation of the solar system and of the earth itself.

The present paper deals only with the transmissive characteristics of these glasses and certain resulting deductions based thereon concerning their formation within the parent meteoric planet. For a general description of tektites found in many locations, reference should be made to the extensive report by Barnes (1940).

## 2. Instruments and Method

The spectral transmittances of the tektite glasses in the ultraviolet, visible, and near-infrared (to 1000 millimicrons) were obtained with a Beckman quartz spectrophotometer (Cary and Beckman, 1940; Gibson and Balcom, 1947). The data are directly comparable from one sample to another, since all the samples were polished to approximately the same thickness (0·5 to 0·6 millimetres). In

a number of cases the sample was too small to fill the complete aperture of the instrument, so that a special diaphragm was placed in the beam to eliminate all radiant energy not passing directly through the sample.

The spectral infrared transmittances were obtained with a Perkin-Elmer double-beam automatic recording instrument. The two beams were similarly diaphragmed for balance at an aperture slightly smaller than the smallest specimen examined.

## 3. Results and Discussion

The spectral data in the ultraviolet and visible (see Figs. 1 to 4) indicate a number of things. The high ultraviolet absorption results primarily from the high iron-

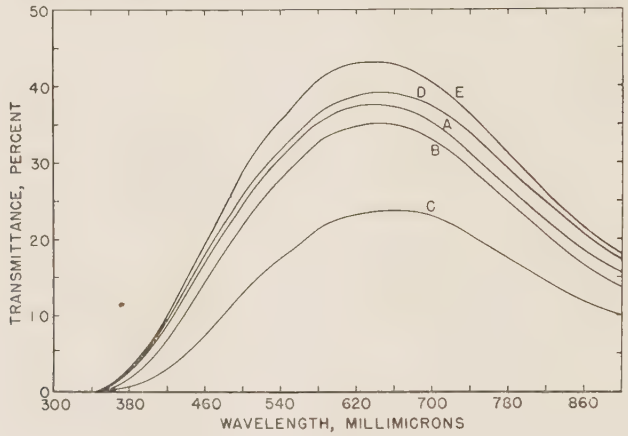


Fig. 1. Spectral transmittances of five australites. Sample A from Cassidy Collection; other from H. H. Nininger.

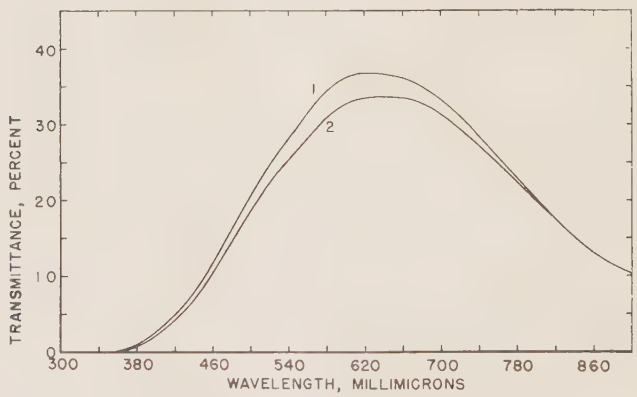


Fig. 2. Spectral transmittances of two Philippine tektites. No. 1 from Santa Mesa, Rizal province; No. 2 from Pugad Babuy, Balakan province.

oxide content of the glass. The colour results principally from the combined absorptions of iron, nickel, chromium, and manganese oxides. Copper, also, may be present in sufficient concentration to assist in the coloration of some of the

samples, although it is not found in the ordinary chemical analyses (BARNES, 1940); see Table 1. The reduced transmittance in the red and near-infrared results primarily from the presence of iron oxides in the glass. The iron has been reported to be principally in the ferrous state (FeO), although the colour in the

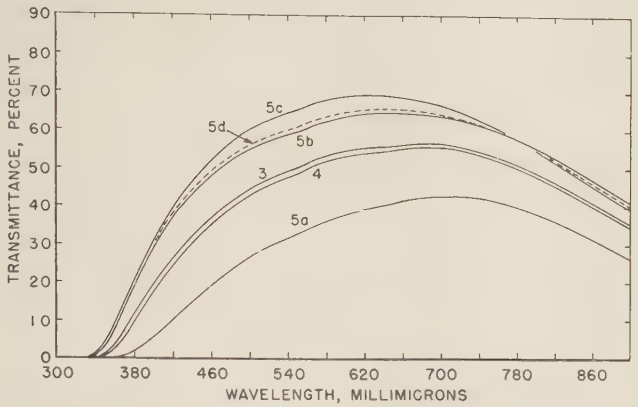


Fig. 3. Spectral transmittances of six bediasites. No. 3 from near Muldoun, Fayette County; No. 4 from eastern portion of Lee County; and 5a, 5b, 5c, and 5d from near Bedias, Grimes County, Texas.

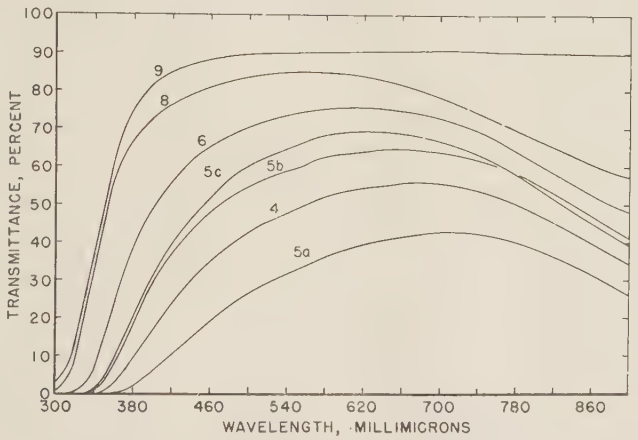


Fig. 4. Spectral transmittances of seven tektites from various sources. No. 9 a Libyan desert glass from Egypt; No. 8 is a moldavite from Radomilic, Bohemia; No. 6 from Empire, Georgia; and the other bediasites from Texas (see Fig. 3).

visible and the relatively high transmittance in the near-infrared might indicate a predominately ferric iron glass (PHILLIPS, 1941).

A comparison between the infrared transmittances of the tektite glasses and that of a number of industrial welding glasses (see Figs. 6, 7, and 8), produced at different times and with different iron-oxide compositions during the past thirty years, is interesting. In one of the earliest industrial welding glasses (see glass *N* of Figs. 5 and 8) little or no iron was added (purposely), hence the near-infrared

transmittance was high. In this case the colour probably results primarily from nickel-oxide and carbon. A similar glass, first produced about twenty-five years ago, included the addition of iron. The resulting glass (see glass *O* of Figs. 5 and 8),

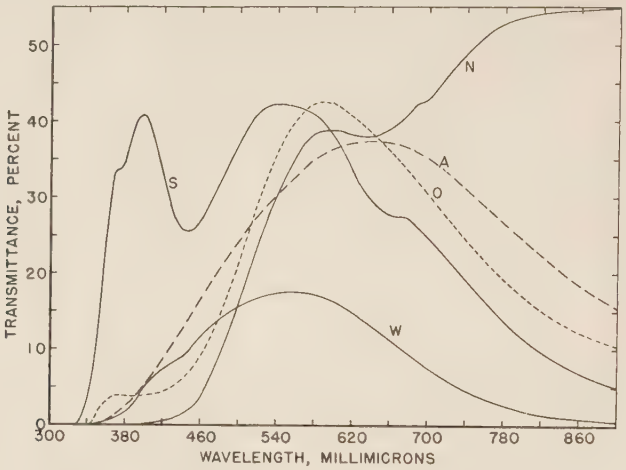


Fig. 5. Spectral transmittances of four samples of welding glass from various sources and times of production. Sample *N*, product of an American manufacturer about 1925; sample *O*, product from same source about 1930; sample *S*, a green glass of somewhat later production (possibly foreign production); and sample *W*, a recent American production having a high reduced iron content. Also australite, sample *A*, from Fig. 1.

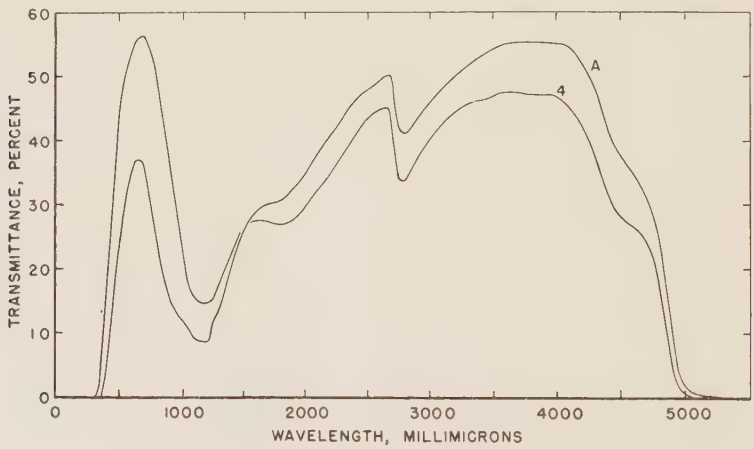


Fig. 6. Spectral infrared transmittances of two tektites. Sample *A*, an australite; sample 4, a bediasite.

no doubt containing a mixture of ferric ($Fe_2O_3$) and ferrous (FeO) iron had infrared transmission characteristics not appreciably different from those of some of the tektites. An industrial glass of slightly later production (see glass *S* in Figs. 5 and 8) had a visible transmittance indicating a higher ferrous oxide (lower ferric) content. However, this glass does not match any of the tektites in either visible

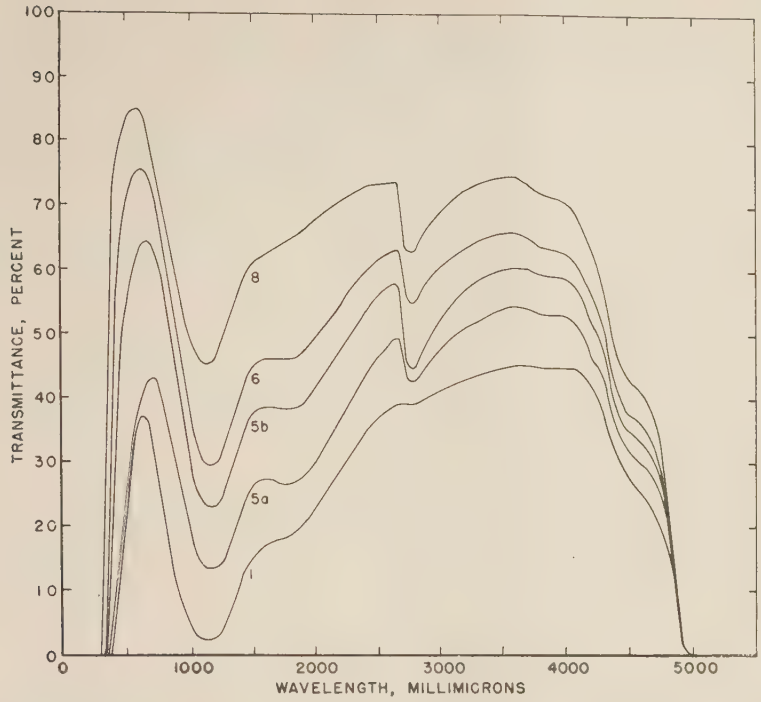


Fig. 7. Spectral infrared transmittances of five tektites from various sources. No. 8, a moldavite; No. 6, a Georgia tektite; Nos. 5a and 5b, Texas bediasites; and No. 1, a Philippine rizalite.

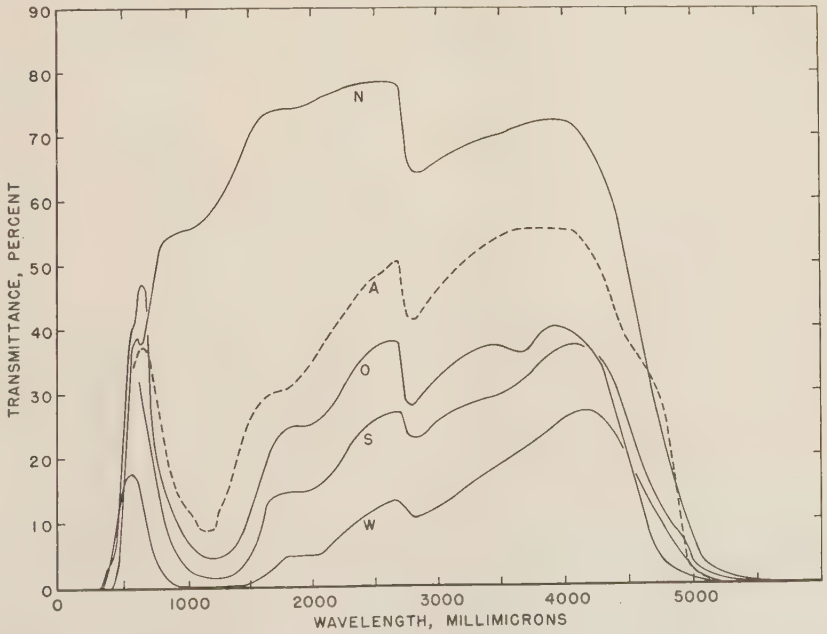


Fig. 8. Spectral infrared transmittances of the four welding glasses (see Fig. 5). Also australite, sample *A*, from Fig. 6.

or infrared transmission characteristics as well as the earlier produced one. A commercial welding glass of recent production (see glass *W* of Figs. 5 and 8) has a colour indicating high relative ferrous-oxide content. It has transmission characteristics somewhat different from those of any of the tektites.

In commercial manufacture, the colour of iron-containing glass depends somewhat upon the base constituents and its subsequent treatment by heat and irradiation, but mostly upon the concentration of iron and its degree of reduction by the furnace atmosphere, including reagents, and the melting temperature (Weyl, 1951; Brewster and Kreidl, 1951; Forrest, etc., 1948; Densem and Turner, 1938). For a base glass of high silica concentration it has been found that as the iron-oxide content, added in the form of $Fe_2O_3$, is increased, the peak in transmittance gradually shifts from the green to the red region of the spectrum, resulting in glasses shading from light greenish yellow to brown in colour (Brewster and Kreidl, 1951). At the same time the optical density increases greatly with the increase in iron content.

The set of tektite transmission curves displayed in Fig. 4 are very similar in shape and magnitude to what would be expected by the addition of iron in commercial glasses in the form of $Fe_2O_3$ (see Fig. 2 of Reference 7). The meaning of

*Table* 1. *Tektite glass compositions, specific gravity, and index of refraction as reported by* Virgil E. Barnes (1940)

| *Glass authority** | *Australites* 58 | *Philippines* 44 | *Bediasites* 16 | *Moldavites* 11 | *Libyan glass* 65 |
|---|---|---|---|---|---|
| $SiO_2$ | 70·62 | 71·20 | 77·76 | 80·73 | 97·58 |
| $Al_2O_3$ | 13·48 | 13·52 | 13·30 | 9·61 | 1·54 |
| $Fe_2O_3$ | 0·85 | 0·59 | 0·37 | — | 0·11 |
| FeO | 4·44 | 3·89 | 3·36 | 1·93 | 0·23 |
| MgO | 2·42 | 2·23 | 1·19 | 1·59 | tr |
| CaO | 3·09 | 3·40 | 0·04 | 2·13 | 0·38 |
| $Na_2O$ | 1·27 | 1·59 | 1·41 | 0·37 | 0·34 |
| $K_2O$ | 2·22 | 1·84 | 1·97 | 3·60 | none |
| $H_2O$ total | 0·07 | 0·63 | 0·02 | 0·02 | 0·10 |
| $TiO_2$ | 0·90 | 0·92 | 0·76 | 0·32 | 0·21 |
| MnO | 0·42 | 0·08 | 0·01 | 0·07 | tr |
| Total % | 99·78 | 99·99 | 100·19 | 100·37 | 100·49 |
| Sp. gr. | 2·454 | 2·436 | 2·357 | 2·343 | 2·208 |
| $N_{Na}$ | — | — | 1·492 | 1·487 | 1·4624 |

* For the original data, reference should be made to the following:

11. R. Nováček (1932) *Casopis Narodniho Musea Praha* **106,** 68. [Lhenice, Bohemia.]
16. Analyst, Gonyer. Minor constituents: NiO, CoO, CuO, none. [Grimes County, Texas.]
44. Cath. M. Koomans (1938) Leidsche Geol. Meded., Deel 10, Afl. 1, 70. Analyst, Koomans. [Philippines, Bulakda.] Total includes $P_2O_5$, 0·10.
58. *Ann. Rept. Secretary Mines, Victoria*, 1907, p. 63, 1908. Analyst not stated. [Coolgardie, West Australia.] Minor constituents: $SO_2$, Cl, NiO, trace; $P_2O_5$, $CO_2$, none.
65. P. A. Clayton and L. J. Spencer (1934) *Mineralog. Mag.*, **23,** 501. Analyst: M. H. Hey. [Libyan Desert, Egypt.] Minor constituent: NiO, trace.

this is a little uncertain, since most of the iron oxide in the tektites has been listed as being in the form of FeO (see Table 1 and Reference 1). The relatively high infrared transmittances of the tektites in the spectral region of 1000 to 2000 millimicrons indicates, furthermore, that much of the iron may be in the unreduced state ($Fe_2O_3$) or in some equivalent combination as regards infrared spectral absorption.

Reduction in commercial glass may be accomplished by an oxygen-deficient atmosphere, the addition of carbon, or by heating the glass at high temperatures.

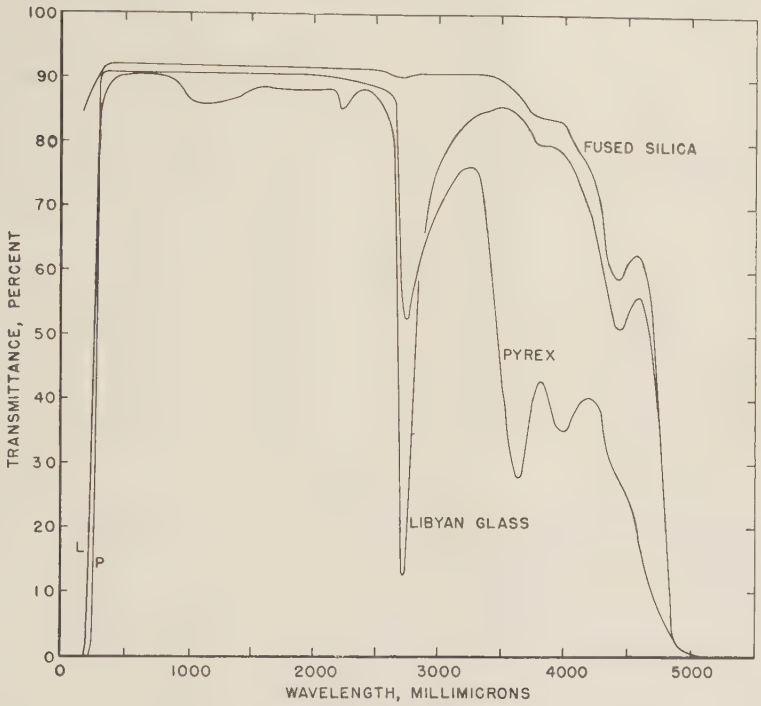


Fig. 9. Spectral infrared transmittances of Libyan desert glass as compared with commercial fused-silica and Pyrex glasses.

In the case of the tektite glasses it appears from their colours and general transmissive properties that reduction of the iron has been retarded. Furthermore, since all tektites examined show complicated flow patterns of inhomogeneity, striae, strain, and often associated variations in colour or optical density, they must have been formed under conditions in which they did not have time to reach an equilibrium state (Brown and Patterson, 1948).

The magnitude of the water and carbon-dioxide absorption at 2800 millimicrons offers a significant clue regarding the conditions under which the tektite glasses were formed. The Philippine tektites (see No. 1 of Fig. 7) show the least selective absorption at this wavelength of any of the samples examined. (Another specimen of this glass showed slightly stronger absorption than existed in the case of No. 1.) All the bediasites had a similar degree of absorption at 2800 millimicrons.

This would indicate a common origin and/or common treatment. It is not known, however, if part of the water contained within the tektites may have been acquired after landing on the earth.

The Libyan desert glass is especially interesting (see Fig. 9). The strong absorption at 2800 millimicrons is not shared by any of the true tektites. A comparison with commercial fused silica and with a high-silica glass (Pyrex 7740) indicates certain similarities with each material, but also significant differences from both. While the ultraviolet and visible transmittances of this glass show slight resemblance to the tektites (see Fig. 4), the infrared data indicate marked differences in composition and in conditions under which the glass was formed.

If the chemical determinations of the compositions of the tektites are correct (Barnes, 1940), then their spectral transmittances may offer a significant clue relative to the temperatures, pressures, type of atmosphere, and to certain other conditions existing on the meteoric planet at the time and place of their formation. Hence, research on the production of similar glasses should furnish valuable information in the solution of some of the cosmological problems facing astronomers, geologists, and meteoriticists today.

The Philippine, Georgia, and moldavite tektites were supplied through the courtesy of E. P. Henderson, Associate Curator of the National Museum; the Texas bediasites by Virgil E. Barnes of the University of Texas; and the australite sample A by Wm. A. Cassidy. The remaining samples of australites were purchased from H. H. Nininger.

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# $A^{40}$-$K^{40}$ dating*

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ABSTRACT

The $A^{40}/K^{40}$ ratios and the Pb-U ages of various co-existing potassium feldspars and uraninites were determined. It was found that with a branching ratio $\lambda_e/\lambda_\beta = 0{\cdot}085 \pm 0{\cdot}005$ and a decay constant $\lambda = 0{\cdot}55 \times 10^{-9}$/yr, the $A^{40}/K^{40}$ ages could be brought into agreement with the Pb-U ages for samples ranging from 260 to 1860 m.y. No evidence was found for the loss of argon by diffusion from potassium feldspars.

## Introduction

The purpose of this investigation was to determine the feasibility of using the radioactive decay of $K^{40}$ into $A^{40}$ as a method of geologic dating. It is generally agreed, at the present time, that the most reliable age determinations are those obtained by the Pb-U method when there is agreement between any two of the $Pb^{206}/U^{238}$, $Pb^{207}/U^{235}$, or $Pb^{206}/Pb^{207}$ ages. In the present work, agreement to within experimental error of the $Pb^{206}/U^{238}$ and $Pb^{207}/U^{235}$ ages has been accepted as the criterion for the true age of the samples studied. In order to test the $A^{40}/K^{40}$ method, it was therefore necessary to compare $A^{40}/K^{40}$ ages with good Pb-U ages.

The age ($\tau$) of a potassium mineral is given by the following expression

$$\tau = \frac{1}{\lambda} \ln \left\{ 1 + \frac{A^{40}}{K^{40}} \frac{(1 + R)}{R} \right\}$$

where $\lambda$ is the total decay constant of $K^{40}$ and is equal to the sum of the $\beta^-$ decay constant ($\lambda_\beta$) and the electron-capture decay constant ($\lambda_e$), $R$ is the branching ratio ($\lambda_e/\lambda_\beta$), and $A^{40}/K^{40}$ is the ratio of the number of radiogenic $A^{40}$ atoms to the number of $K^{40}$ atoms now present.

The total decay constant of $K^{40}$ is essentially determined by the rate of $\beta$ -emission because of the relatively small number of electron captures. The $\beta^-$ decay constant has been determined by a number of workers with satisfactory agreement (F. Birch, 1951). There is, however, considerable uncertainty in $\lambda_e$ and it is therefore not possible to make a direct comparison of the Pb-U and $A^{40}/K^{40}$ dating methods. If, however, it is possible to find a unique value for the branching ratio such that the calculated $A^{40}/K^{40}$ ages agree with the Pb-U ages for samples covering a wide span of geologic time, it is then clear that the argon method is applicable. Since it was assumed that this method is absolute, the value

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of the branching ratio so obtained should agree with the value of $\lambda_e/\lambda_\beta$ determined by a precise counting experiment.

The present work proposes to show that with a branching ratio of 0·085, $A^{40}/K^{40}$ ages can be obtained which agree quite well with Pb-U ages for samples ranging in age from 260 m.y. to 1860 m.y.

It was expected that the argon method would yield better results than the helium method because of the negligible radiation damage incurred in potassium minerals due to $K^{40}$ decay and because the much larger atomic radius of argon compared with that of helium should result in less diffusion loss.

## Method

The feldspar to be analyzed was ground, and a convenient sieve fraction taken. Samples for the argon and potassium analyses were taken from this fraction by using a small sample splitter. The potassium analyses were done by K. Jensen of the Argonne National Laboratory. The

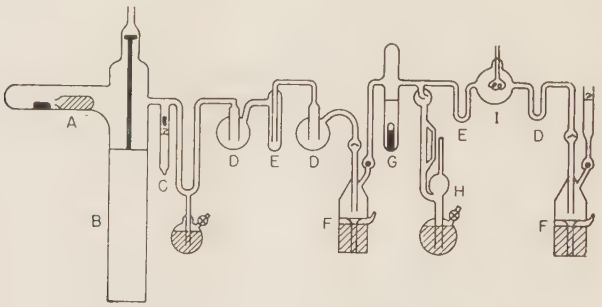


Fig. 1. Argon extraction apparatus.

*A*. Sample and iron slug.
*B*. Nickel furnace.
*C*. $A^{38}$ tracer.
*D*. Cold trap.
*E*. CuO furnace.
*F*. Toepler pump.
*G*. Calcium furnace.
*H*. McLeod.
*I*. Tungsten filament.

samples were dissolved in aqueous HF and perchloric acids. The potassium was separated by an ethyl acetate extraction and weighed as the perchlorate. The $KClO_4$ was analyzed for rubidium, and the final results were corrected.* A sample of potassium feldspar, obtained from the Bureau of Standards, was analyzed along with each batch of samples for control. The agreement obtained on this standard was better than 1 per cent.

The radiogenic argon content was determined by an isotopic dilution technique (Inghram, 1953, 1954). An aliquot of the feldspar enclosed in a thin-walled Pyrex tube was inserted in the glass side-arm of the nickel reaction vessel (see Fig. 1). The system was evacuated and outgassed until a satisfactory vacuum (less than $10^{-6}$ mm Hg) was achieved. The reaction vessel was then isolated by use of mercury valves, which were used throughout the vacuum system. The sample was then pushed into the furnace, and the $A^{38}$ tracer introduced. The nickel furnace containing NaOH was heated for twenty-four hours at 600°C. At the end of this time the evolved gases were passed through a CuO furnace at 500°C to convert $H_2$ to $H_2O$. The $H_2O$ was condensed in a cold trap, and the remaining gases were transferred to a calcium furnace. The furnace consisted of a stainless-steel crucible containing calcium metal, enclosed in a quartz tube. The

* The possibility of Rb contamination in the perchlorate method was pointed out to the authors by O. Joensuu.

calcium furnace was heated by an external resistance furnace until a mirror was formed. The pressure was then measured with a McLeod gauge. The gas was then allowed to pass through a hot tungsten-filament lamp, CuO at 500°C, and a cold trap. The calcium-furnace and tungsten-filament treatments were repeated until optimum cleanup was obtained. The sample of rare gas remaining was then transferred by means of a Toepler pump to a sample tube and placed on the sample system of the mass spectrometer.

The mass spectrometer used has a 12-inch radius of curvature and a 60° deflection. A low background was obtained in the mass region of interest by frequent baking without opening the instrument to atmospheric pressure. With good sample cleanup, no hydrocarbons were observed at mass 36, 38, or 40 when the sample tube was kept at liquid-nitrogen temperature. On the few occasions when hydrocarbons were observed the resolution of the instrument was sufficient to completely separate them from the argon. It was not possible to resolve the $A^{36}$ and $A^{38}$ peaks from HCl, and hence, care was taken to avoid any contamination with chlorine.

In order to correct for discrimination, normal argon was run before and after each radiogenic sample, and the discrimination was calculated from the observed $A^{36}/A^{40}$ ratio in the normal. Nier's values (Nier, 1950) for the isotopic composition of normal argon were assumed. The amount of radiogenic $A^{40}$ extracted from the feldspar was computed from the observed $A^{36}/A^{38}$ and $A^{38}/A^{40}$ ratios and from the known volume of $A^{38}$ tracer which had been added. It was assumed that the peak at mass 36 was due to normal argon contamination. In most cases 95 per cent or more of the argon analyzed was radiogenic.

The lead, uranium, and thorium analyses of the uraninites were done by K. Jensen of the Argonne National Laboratory. The lead was separated by electro-deposition as $PbO_2$ from a nitric-acid solution. The thorium was separated by solvent extraction from the uranium and rare earths and weighed as $ThO_2$. The uranium was separated from the rare earths by an ether extraction and weighed as $U_3O_8$.

The lead isotopic composition of the uraninites was determined by using a surface ionization technique with a 12-inch mass spectrometer which was similar to the gas instrument. $Pb^+$ ions were formed by surface ionization from a tungsten filament which had been loaded with $Pb(NO_3)_2$ in a borax binder. This procedure is described by Tilton *et al.* (in press).

## Tracer Preparation

$A^{38}$ was obtained by neutron irradiation of NaCl.* The argon was extracted from the salt by melting in an evacuated vessel. The gases were then purified, and the $A^{38}$ was transferred to the tracer line (see Fig. 2). The tracer line consisted of a series of interconnecting capillary Y tubes which were connected to a mercury reservoir. Break-off tubes of known volumes were attached

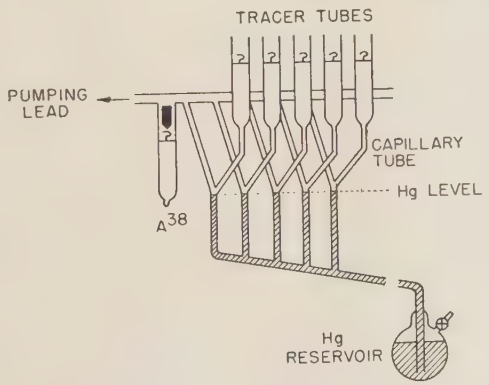


Fig. 2. Tracer preparation line.

* $A^{38}$ tracer later became available from the Oak Ridge National Laboratory. This was used in the latter part of this work.

*Table 1. Microcline, Bessner Mine, Lot 5, Con. B, Henvey Twp., Ontario*

| *Experiment* | *Sample Wt. (gm)* | *Sieve fraction* | %K | $A^{38}$ *tracer (cc STP)* | $A^{38}/A^{40}$ | $A^{36}/A^{38}$ | *Radiogenic* $A^{40}$*(cc STP) per g* | $A^{40}/K^{40}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 14·522 | 40–80 | 11·00 | 1·210 $\pm$ 0·02 $\times 10^{-5}$ | 1·92 $\pm$ 0·02 $\times 10^{-3}$ | 0·0506 $\pm$ 0·001 | 4·25 $\pm$ 0·12 $\times 10^{-4}$ | 0·0565 $\pm$ 0·0014 |
| 2 | 27·283 | 18–40 | 10·92 | 1·055 $\pm$ 0·02 $\times 10^{-5}$ | 9·03 $\pm$ 0·1 $\times 10^{-4}$ | 0·044 $\pm$ 0·001 | 4·27 $\pm$ 0·12 $\times 10^{-4}$ | 0·0573 $\pm$ 0·0014 |
| 3 | 6·902 | 18–40 | 10·92 | 1·125 $\pm$ 0·02 $\times 10^{-5}$ | 3·72 $\pm$ 0·02 $\times 10^{-3}$ | 0·032 $\pm$ 0·001 | 4·22 $\pm$ 0·12 $\times 10^{-4}$ | 0·0567 $\pm$ 0·0014 |
| 4 | 16·444 | 80–180 | 10·43 | 1·111 $\pm$ 0·02 $\times 10^{-5}$ | 1·73 $\pm$ 0·01 $\times 10^{-3}$ | 0·0279 $\pm$ 0·0001 | 3·85 $\pm$ 0·12 $\times 10^{-4}$ | 0·0542 $\pm$ 0·0014 |

*Table 2.*

| *Locality* | *No.* | *Sample Wt. (gm)* | %K | $A^{38}/A^{40}$ | $A^{36}/A^{38}$ | $A^{38}$ *tracer* (*cc STP*) $\times 10^{+5}$ | $A^{40}/K^{40}$ | Pb-U *age* (*yrs.*) | $\lambda_e/\lambda_\beta$ | $A^{40}/K^{40}$ *age for* $\lambda_e/\lambda_\beta = 0{\cdot}085$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Strickland Quarry (Collins Hill), Portland, Conn. | 1 | 22·904 | 10·51 ± 0·02 | 0·01603 ± 0·00004 | 0·0074 ± 0·0020 | 3·483 | 0·01282 | $2{\cdot}67 \times 10^8$ | 0·0894 | $2{\cdot}74 \times 10^8$ |
| Blackstone Lake Pit Conger Twp., Parry Sound, Ontario | 2 | 16·701 | 11·98 ± 0·02 | 0·001475 ± 0·00001 | 0·056 ± 0·003 | 1·136 | 0·0556 | $9{\cdot}94 \times 10^8$ | 0·0827 | $9{\cdot}75 \times 10^8$ |
| | | 12·472 | 11·98 ± 0·02 | 0·00196 ± 0·00001 | 0·120 ± 0·002 | 1·141 | 0·0543 | $9{\cdot}94 \times 10^8$ | 0·0806 | $9{\cdot}57 \times 10^8$ |
| | 3 | 28·177 | 1·32 ± 0·03 | 0·0282 ± 0·0004 | 0·0124 ± 0·0010 | 3·611 | 0·0456 | $9{\cdot}94 \times 10^8$ | 0·0660 | $8{\cdot}34 \times 10^8$ |
| | 4 | 37·439 | 10·62 ± 0·02 | 0·00229 ± 0·00003 | 0·0348 ± 0·0020 | 3·739 | 0·0592 | $9{\cdot}94 \times 10^8$ | 0·0886 | $1{\cdot}02 \times 10^9$ |
| Concession XVI Cardiff Twp., Ontario | 5 | 24·778 | 3·02 ± 0·06 | 0·00995 ± 0·00003 | 0·0436 ± 0·0020 | 3·624 | 0·0629 | $1{\cdot}01 \times 10^9$ | 0·0926 | $1{\cdot}07 \times 10^9$ |
| | 6 | 34·026 | 4·79 ± 0·05 | 0·00553 ± 0·00004 | 0·0314 ± 0·0020 | 3·779 | 0·0587 | $1{\cdot}01 \times 10^9$ | 0·0858 | $1{\cdot}02 \times 10^9$ |
| Tory Hill, Ontario | 7 | 12·065 | 6·15 ± 0·02 | 0·00368 ± 0·00004 | 0·0303 ± 0·0010 | 1·035 | 0·0540 | $1{\cdot}03 \times 10^9$ | 0·0763 | $9{\cdot}53 \times 10^8$ |
| | 8 | 32·729 | 6·86 ± 0·04 | 0·00428 ± 0·00002 | 0·0146 ± 0·0008 | 3·605 | 0·0542 | $1{\cdot}03 \times 10^9$ | 0·0765 | $9{\cdot}55 \times 10^8$ |
| Viking Lake, Beaverlodge Dist., Saskatchewan | 9 | 24·516 | 11·68 ± 0·02 | 0·00298 ± 0·00004 | 0·0196 ± 0·0004 | 8·859 | 0·1502 | $1{\cdot}87 \times 10^9$ | 0·0912 | $1{\cdot}95 \times 10^9$ |

*Table 3. Ages of uraninites (yrs.)*

| *Material* | *Locality* | % Pb | % U | % Th | $\frac{207}{206}$ | $\frac{208}{206}$ | $\frac{204}{206}$ | $\frac{Pb^{206}}{U^{238}}$ | $\frac{Pb^{207}}{U^{235}}$ | $\frac{Pb^{208}}{Th^{232}}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Uraninite | Viking Lake, Beaverlodge Dist., Sask. | 17·14 | 52·9 | 5·24 | 0·1155 ± 0·0020 | 0·0290 ± 0·0004 | 0·000057 | $1·85 \times 10^9$ | $1·88 \times 10^9$ | $1·67 \times 10^9$ |
| Uraninite | Blackstone Lake Pit, Conger Twp., Parry Sound, Ont. | 10·72 | 69·3 | 2·99 | 0·0724 ± 0·0008 | 0·0150 ± 0·0002 | 0·000075 | $9·94 \times 10^8$ | $9·93 \times 10^8$ | $8·97 \times 10^8$ |
| Uraninite | Pit in Con. XVI Cardiff Twp. Ont. | 9·92 | 62·3 | 6·61 | 0·0749 ± 0·0004 | 0·0346 ± 0·0003 | 0·00015 | $1·00 \times 10^9$ | $1·02 \times 10^9$ | $0·87 \times 10^9$ |
| Uraninite | Strickland Quarry Portland, Conn. | 3·07 | 79·1 | 2·98 | 0·0529 ± 0·00035 | 0·0160 ± 0·00015 | 0·000139 | $2·68 \times 10^8$ | $2·66 \times 10^8$ | $2·39 \times 10^8$ |

to the apparatus, and the system was evacuated. The system was then sealed off, and the $A^{38}$ introduced. The mercury level was adjusted to a point immediately below the junction of the Y's. The gas was allowed to equilibrate for twelve hours, after which the mercury level was raised to isolate the tubes. The tracer tubes were then sealed off. Corrections were made for the volume of capillary between the tracer tube and the Y and for the gas trapped between the mercury and the point of sealing off.

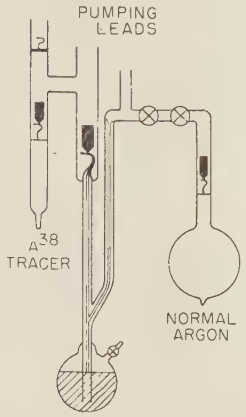


Fig. 3. Capillary pipette and tracer equilibration apparatus.

The tracers were calibrated by an isotopic dilution with a known volume of normal argon of spectroscopic purity. The volume of normal argon was measured at a known temperature in a capillary pipette with a break-off top (see Fig. 3). The volume of normal argon was then mixed with the argon from one of the previously prepared tracers by breaking the break-off end of the pipette. After sufficient time for equilibration was allowed, a mass spectrometric analysis was made of the argon mixture, and the volume of $A^{38}$ in the tracer was computed from the $A^{36}/A^{38}$ ratio. The discrimination of the spectrometer was determined from the $A^{36}/A^{40}$ ratio. The amount of $A^{38}$ in the remaining tracers was then computed by assuming that the pressure in the tracer line was everywhere equal.

## Experimental Results

In order to test the method, four samples of microcline from Bessner, Ontario, were analyzed. The samples were taken from various sieve fractions. The results agree with each other within experimental error (see Table 1). The $A^{40}/K^{40}$ ratio obtained in run 4 is slightly lower than that obtained in the other experiments. This is possibly due to argon loss because of grinding.

In runs 1 and 2, the reaction and tracer equilibration time was twenty-four hours. In run 3, the reaction time was twenty-four hours and the equilibration time twelve hours. In run 4, the reaction and tracer equilibration time was thirty-four hours. The results indicate that the time allowed for tracer equilibration was sufficient. The agreement for different reaction times and sieve fractions suggests that the reaction was complete.

The values given in Table 1 for the volume of $A^{38}$ tracer and the $A^{40}/K^{40}$ ratio differ from those reported previously by Wasserburg and Hayden (1954) by 6 per cent. The earlier values are incorrect owing to an error in tracer calibration.

The errors listed in the tracer-volume determination are the probable error of the isotopic ratios and the estimated errors.

A sample of Bessner microcline was also run with $Na_2CO_3$ as a flux in order to determine if more argon would be released by other fluxing methods. The material was reacted for eight hours at slightly over 900°C. The radiogenic argon yield was 12 per cent less than that obtained with NaOH. Because there was a large amount of normal argon contamination in the $Na_2CO_3$ experiment, this discrepancy may not be real.

Table 2 gives the results obtained for samples from several different localities. All samples were extremely fresh, large pegmatitic feldspars with the exception of No. 8, which was a sample of granite.

Samples No. 2 and No. 3 were from the same pegmatite. Sample No. 4 was from part of the same pegmatite complex as No. 2 and No. 3. Sample No. 4 was collected from an outcrop one mile north of Blackstone Lake Pit. Sample No. 3 has a factor 10 less potassium than No. 2 and No. 4. The reason for the low $A^{40}/K^{40}$ ratio in No. 3 is unknown. Samples No. 5 and No. 6 were from the same pegmatite dike. Although they differ in potassium content by 60 per cent, their $A^{40}/K^{40}$ ratios are in good agreement.

Sample No. 7 is from a feldspar crystal in a pegmatite dike cutting a paragneiss complex one mile north of Tory Hill, Ontario. This pegmatite is one of many pegmatitic bodies surrounding the granite body at Essonville, Ontario, and it is presumably, although not certainly, of the same age as the Essonville granite body immediately to the north of Tory Hill. Sample No. 8 is from the eastern flank of this granite body. It is a highly deformed granite with a distinct planar structure due to the presence of tabular quartz grains. There was no mica present in the specimen which was analyzed.

Lead-uranium-thorium ages were determined for uraninites associated with the various feldspars. The samples were fresh material with no alteration products present. The results are given in Table 3. The last three columns are the calculated $Pb^{206}/U^{238}$, $Pb^{207}/U^{235}$, and $Pb^{208}/Th^{232}$ ages, respectively. The values of the decay constants used in the calculations were: $\lambda Th^{232} = 4{\cdot}99 \times 10^{-11}\ yr^{-1}$; $\lambda U^{238} = 1{\cdot}54 \times 10^{-10}\ yr^{-1}$; and $\lambda U^{235} = 9{\cdot}72 \times 10^{-10}\ yr^{-1}$. The $U^{238}/U^{235}$ ratio was assumed to be 137·7.

In all cases excellent agreement between the $Pb^{206}/U^{238}$ and $Pb^{207}/U^{235}$ ages was obtained. The $Pb^{208}/Th^{232}$ ages were consistently low by about 10 per cent.

The Viking Lake area, which has not previously been dated, gives ages a few per cent higher than the $Pb^{207}/Pb^{206}$ ages reported by Russell *et al.* (1953) for Charlebois Lake, Sickle Lake, and Lee Lake, Saskatchewan.

The results obtained for the Conger Township material agree with the data of Nier (1941). The Cardiff Township dates are also in accord with the results of Nier (1939) and Collins *et al.* (1953).

The ages which we have determined for Strickland Quarry are slightly lower than the chemical ages reported by several other workers for this locality (Rodgers, 1952). They agree within 5 per cent with the Spinelli Quarry dates obtained by Nier (1941) and show that the Spinelli and Strickland Quarries are of essentially the same age, as suggested by Rodgers (1952).

The age given for samples No. 7 and No. 8 of Table 2 is taken from the data of Tilton *et al.* (in press). They were determined on zircons taken from the same

granite body as No. 8. The $Pb^{206}/U^{238}$ and $Pb^{207}/U^{235}$ ages which they obtained are $1{\cdot}06 \times 10^9$ and $1{\cdot}03 \times 10^9$ years, respectively.

The $A^{40}/K^{40}$ ages calculated for these samples by using a branching ratio of 0·126 (Faust, 1950; Sawyer and Wiedenbeck, 1949, 1950; P. R. J. Burch, 1953; Inghram *et al.*, 1950; Houtermans *et al.*, 1950) and a decay constant $\lambda = 0{\cdot}55 \times 10^{-9}$ yr$^{-1}$ are consistently low as compared to the Pb-U ages. Column 10 of Table 2 gives the calculated branching ratio for each sample assuming the Pb-U age. It is seen that the spread in the calculated value is between 0·076 and 0·093 with the exception of sample No. 3. Sample No. 3 was not used in the final branching ratio calculation because it was felt that this was anamolously low due to argon loss. An X-ray diffraction picture of sample No. 3 shows it to be an albite. All other samples were microclines.* The low argon content may be in some way related to this. The sample from Bessner, Ontario, was not used in calculating the branching ratio because of the great uncertainty in its age (Wasserburg and Hayden, 1954; Shillibeer *et al.*, 1954).

Column 6 of Table 2 gives the $A^{40}/K^{40}$ age calculated with a branching ratio of 0·085. This value brings the $A^{40}/K^{40}$ ages into good agreement with the Pb-U ages over a considerable range of geologic time.

The $A^{40}/K^{40}$ age calculated for the Bessner sample by using the above branching ratio is $9{\cdot}94 \times 10^8$ years. This value is in agreement with the $Pb^{207}/Pb^{206}$ age of $9{\cdot}4 \pm 0{\cdot}5 \times 10^8$ years determined by Russell *et al.* (1953).

The value of 0·085 is considerably lower than the values of 0·11 to 0·13 reported by other workers (Faust, 1950; Sawyer and Wiedenbeck, 1949, 1950; P. R. J. Burch, 1953; Inghram *et al.*, 1950; Houtermans *et al.*, 1950). More recent data obtained by Suttle and Libby (in press) give a branching ratio of $0{\cdot}10 \pm 0{\cdot}01$ and a decay constant $\lambda = 0{\cdot}56 \times 10^{-9}$ yr$^{-1}$. Sawyer and Wiedenbeck (1949, 1950) using $K^{42}$ to calibrate their scintillation counter, obtained a branching ratio of 0·127. The value for the percent gamma yield of $K^{42}$ which they used was 25 per cent. As pointed out by Houtermans *et al.* (1950), a more recent determination by Siegbahn gave a value of $16 \pm 4$ per cent. Kahn and Lyon (1953) have remeasured the gamma yield for $K^{42}$ and obtained a value of $20 \pm 1$ per cent. By recalculating the data of Sawyer and Wiedenbeck and using Kahn's value of 20 per cent, a branching ratio of $0{\cdot}102 \pm 0{\cdot}01$ is obtained.†

It is evident from the above data that a more precise determination of the decay constants of $K^{40}$ by counting methods is needed.

It is not at present possible to distinguish between small systematic diffusion loss of radiogenic argon and a small change in the branching ratio. However, as there is no apparent trend in the calculated branching ratio with time, and because of the good agreement obtained for significantly different samples of the same age, we feel that there is no evidence for loss of argon due to diffusion.

Gentner *et al.* (1953) have reported a value of $D = 10^{-19}$ cm$^2$/sec for argon in sylvite. Recent data by Chemla (1954) give a calculated value of $D = 10^{-31}$ cm$^2$/sec for the diffusion coefficient of $Na^+$ in NaCl at 20°C. The data for sodium were determined in the temperature range from 600°C to 700°C. Although

* J. R. Goldsmith, private communication.

† The authors are indebted to R. D. Russell for calling this to their attention.

structural defects due to radiation damage may account for the much larger diffusion coefficient for argon, it is none the less somewhat difficult to reconcile these two results. If the diffusion constant for argon in feldspar were of the same order of magnitude as that reported for argon in sylvite, the effects of diffusion should have been detected in our experiments.

## Conclusions

With a branching ratio of 0·085 and a decay constant $\lambda = 0{\cdot}55 \times 10^{-9}\,\mathrm{yr}^{-1}$, $A^{40}/K^{40}$ ages are obtained which agree with Pb-U ages within a few per cent for a considerable span of geologic time. These results indicate that a precise determination of the geologic age of potassium feldspars may be obtained by the $A^{40}/K^{40}$ method. It should be possible to determine the age of feldspars as young as $2 \times 10^7$ years by the technique described, without any loss in precision.

The agreement obtained by the two methods, one of which depends on the rate of alpha-emission and the other of which depends on the rate of beta-emission and electron capture, places a rather strict limitation on the possible time dependence of the universal constants involved (Houtermans *et al.*, 1946).

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# Theoretical effect of diffusion on isotopic abundance ratios in rocks and associated fluids*

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ABSTRACT

Diffusion is considered as a possible process of isotope fractionation taking place throughout geologic time. Both diffusion in solids and diffusion in liquids are taken as possible mechanisms, the latter being more important. Arguments are presented to show that if significant fractionation takes place within a crystal by outward diffusion under solid-state conditions, enrichment will be evident only in elements of minor concentration. Similar conclusions are inferred for solid-state diffusion across a boundary or for diffusion in liquids. No isotopic enrichment can be expected in relatively large bodies of diffusion transported material. Although the necessary data to confirm these conclusions are scanty, it seems worth while to undertake further work in this direction.

## Introduction

Processes of formation and alteration of rocks that have taken place during geologic time have altered the isotopic abundance ratios of the elements in the earth's crust. The truth of this statement has become increasingly evident during the past decade, as more and more isotopic abundances of several elements have been measured in natural specimens, and significant variations have been noted (Ingerson, 1953; Jensen, 1953).

One of the processes which can cause isotopic fractionation is that of diffusion. Although there is some doubt at the present time as to the relative importance of diffusion as a geological mechanism of rock alteration, there is a strong belief among some geologists and geochemists (Ramberg, 1952) that diffusion may be a major method of material transfer over a period of geologic time. It would seem, therefore, that some of the observed isotopic fractionation found in certain geologic materials might be ascribed to diffusion.

When two or more isotopes of a specific element are transferred by a process of diffusion, a change in isotopic abundance ratio would be expected because of the velocity difference of isotopes of a given element. Where the diffusing material is transported over significant distances a substantial variation in abundance ratios can occur. It is the purpose of this paper to develop the theoretical framework of diffusion as a mechanism of isotope separation in natural materials.

## Diffusion—A Geological Process

Diffusion is a process by which molecules, atoms, or ions, driven by a chemical potential gradient, move from point to point in a solvent phase. The rate of change of concentration with distance is expressed by Fick's Second Law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right) \qquad (1)$$

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where $C$ is the concentration of the diffusing solute, $x$ is the distance, $t$ is the time, and $D$ is the diffusion coefficient.

In considering diffusion as a geologic process it is important to distinguish between solid- and liquid-solvent phases. The term solid-state diffusion generally includes the processes in which the solute diffuses through a solid matrix, along grain boundaries or over surfaces. The present meagre experimental data indicate that grain-boundary and surface diffusion in ionic crystal aggregates are relatively important compared to lattice diffusion through a crystal, especially at moderately low temperatures ($<300°C$). As many rocks may consist of an assemblage of crystals having a large overall area, one might expect that diffusion through the lattice will be much less important than migration along surfaces. For the purposes of this paper, however, solid-state diffusion is taken to mean the result of all three processes unless otherwise specified, because little is known of these individual processes in geologic materials.

Liquid or solute diffusion refers to diffusion of the solute through a liquid, and here its meaning is confined to the diffusion of molecules, ions, or atoms in static-fluid solutions held intergranularly in saturated rocks.

In both types of diffusion isotopic fractionation can occur, but to a different extent and with different limitations. The diffusion coefficients in liquids are larger than the solid-state diffusion coefficients by several orders of magnitude. Consequently, solid-state diffusion can apply only to short-distance phenomena and is operative under geologic circumstances quite different from those supporting diffusion through liquids. Although both processes often occur simultaneously, for the sake of clarity each type is considered separately as an isotope-fractionation process.

A third type of diffusion, thermal, or "Soret" diffusion, is frequently used in the laboratory for isotope fractionation, particularly in a gas phase. As a significant geologic process, however, it is probably not very important. Lovering (1950) has compared the temperature distribution adjacent to a vein with the diffusion fronts. The results of his calculations show that, since the heat conductivities are so much larger than ionic or molecular diffusion coefficients, diffusion takes place under nearly isothermal conditions. As an isotope-fractionation process, then, thermal diffusion is not considered important.

Although there has been a certain amount of disagreement as to the geological importance of diffusion, there are several experimental investigations (Urey *et al.*, 1951; Garrels *et al.*, 1949; Jensen, 1951), which indicate that significant material transfer does take place through geologic time. Also from what is known of the laws of diffusion and of geologic conditions such as temperatures, it is almost certain that significant diffusion did take place.

For instance, consider a hydrothermal fluid containing zinc moving through a fissure cutting a granitic body containing interstitial water. At the time of injection the initial solution will undoubtedly fill the open spaces and pores adjacent to the main fissure because of the existing pressure gradient and capillary action. After gross circulation and mass flow of the solution has ceased, zinc ions would start to migrate integranularly by solute diffusion away from the fissure. Because the temperature is high, and because the concentration equilibrium is

disturbed, ions also start to migrate by diffusion through the lattice from crystal grains into the intergranular solutions and also from the solutions into the crystal grains.

Assuming the above conditions as a reasonable example, it is appropriate to consider a hypothetical case of diffusing atoms or ions at an interface under "semi-infinite" conditions. The concentration at any distance $x$ from the interface is given by

$$C_x = C_0 \left(1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}}\right) \tag{2}$$

where $C_0$ is the concentration of the diffusing atom or ion at the interface, $x$ is the distance from the interface, $D$ is the average diffusion coefficient, and $t$ is the time.* If one arbitrarily chooses $\sqrt{Dt}$ as 10 cm, then the change in concentration with distance is shown in curve Ia of Fig. 1. Any larger value of $\sqrt{Dt}$, such as $\sqrt{Dt} = 50$ cm (Curve IIa), will increase the value of $x$ proportionally for a given value of $C$.

If we further assume that the diffusing atoms comprise light and heavy isotopes of masses $M_L$ and $M_H$, for example masses 103 and 105, having diffusion coefficients $D_L$ and $D_H$, respectively, then

$$\frac{D_L}{D_H} = \sqrt{\frac{M_H}{M_L}} = k$$

$$= \sqrt{\frac{105}{103}} = 1{\cdot}0097 \tag{3}$$

The isotope enrichment, $x$ cm, from the interface is thus

$$S = \left(\frac{C_L C_{H_0}}{C_H C_{L_0}} - 1\right) . 10^2$$

$$= \left(\left\{\frac{1 - \operatorname{erf} \dfrac{x}{2\sqrt{kD_H t}}}{1 - \operatorname{erf} \dfrac{x}{2\sqrt{D_H t}}}\right\} - 1\right) . 10^2 \tag{4}$$

where the zero subscript refers to the original concentrations. Curve Ib (Fig. 1) is the enrichment as a function of $x$ for this hypothetical case, that is, $\sqrt{Dt} = 10$ cm, $k = 1{\cdot}0097$. As the value of $k$ differs from unity for two isotopes of nearly the same mass, and as there is a one-to-one correspondence between $x$ and $\sqrt{Dt}$, then the relation between the Curves Ia and Ib (Fig. 1) will be almost the same as that for any other case regardless of the value of $\sqrt{Dt}$ and $k$.

Both the concentration and isotopic enrichment at any point is a function of the diffusion distance (equations 2 and 4), and little isotopic enrichment can be expected until the concentration drops to less than a 0·1 of the concentration

* Values of the error function (erf) are tabulated in *Tables of Probability Functions*, 1941.

in the source material. This means that one cannot expect significant isotopic enrichment to take place except at a low-concentration diffusion front, and the effect will only be evident in a small amount of material. In the above-cited example of a hydrothermal zinc solution, significant isotopic enrichment of the lighter isotopes would be expected in the small amount of zinc in the diffusion

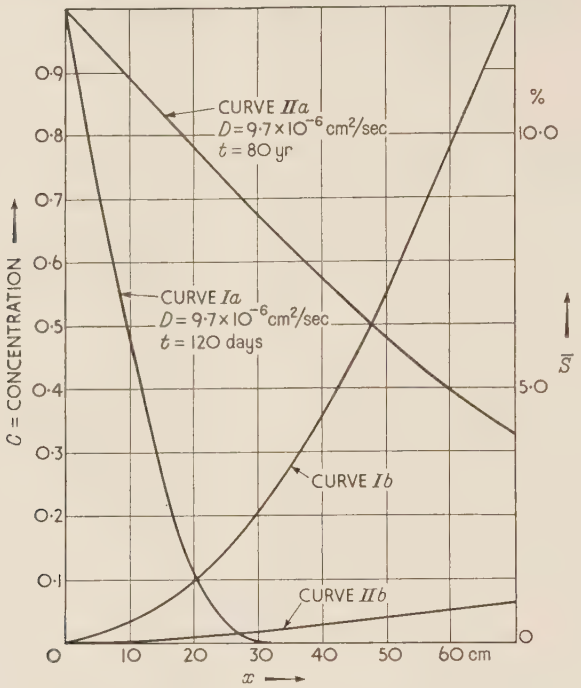


Fig. 1. Curves Ia and IIa: Concentration as a function of distance for a hypothetical element in 120 days and 80 years. Curves Ib and IIb: Percent isotope enrichment as a function of distance under the same conditions and for $k = 1{\cdot}0097$.

fronts containing concentrations of the order of 0·1 or less of the concentration found in the fissure. Thus, most of the diffusion-transported material will not display any significant isotopic enrichment, except possibly where trace quantities of an enriched element in a diffusion front have been removed by some natural process and subsequently concentrated at a particular site. This possibility is discussed below.

## Solid-state Diffusion

Two circumstances of solid-state diffusion of particular interest to the geologist are: Fractionation due to diffusion of an element from a given specimen or crystal; and diffusional effects across a boundary such as a vein-host rock interface.

### *Isotope fractionation due to diffusion in a "spherical crystal"*

In systems where long periods of geologic time are involved and where somewhat elevated temperatures may prevail, it is conceivable that an isotopic separation of several percent might be obtained, especially in small crystals. However, to obtain significant changes in the isotopic-abundance ratio of a given element,

a relatively large fraction of this element must have diffused out of the original crystal, leaving a small remaining fraction enriched in the heavy isotopes. Such a transfer of material must be accompanied by a migration of foreign isotopes to the crystal, i.e., replacement. It is possible by replacement processes for a relatively large amount of a given element to leave a body without destroying the general crystalline texture. Isotopic enrichment of the heavier isotope in a given element with regard to the quantity of material moved, then, could be expected in crystals displaying metasomatism, assuming that replacement took place by solid-state diffusion and not by recrystallization or some other process.

As an example consider the process of replacement of sphalerite by covellite

$$ZnS + CuSO_4 = CuS + ZnSO_4.$$

Copper in interstitial water finds access to the inner parts of the sphalerite. It seems reasonable to assume that both the flow of the copper-bearing solutions and also diffusion of the copper in these solutions will account for the transport of the copper atoms up to the sphalerite grains, but transport within the sphalerite will take place by lattice diffusion. During the process of replacement copper diffuses into the sphalerite crystals and zinc diffuses out in a counter-current process. If almost complete replacement of a grain or crystal is caused by a solid-state diffusion process, the small amount of zinc remaining in the crystals will be enriched in the slow-moving or heavy isotope, while at the same time there will be an enrichment of the lighter isotope of copper within the crystals.

The average enrichment within the crystals of the lighter incoming isotopes (copper in this example) would probably not be significant except in the initial stages of diffusion. In the early stages only a minute amount of copper will have entered the sphalerite crystals, and in the later stages so much copper will have diffused into the sphalerite that the average enrichment of the lighter isotopes will be insignificant. Hence, in the following discussion only enrichment of the heavier isotopes in the small amount of residual element left in a replacement crystal is considered.

It is therefore desirable to investigate what the average isotope fractionation might be within a body, such as a crystal, due to the diffusion of nuclides of different masses out of the crystal. In order to reduce the mathematical manipulations, Bracken and Senftle (1954) have treated the problem for a spherical body. Assuming a spherical crystal and using their qualifying assumptions, the mean percent enrichment, $\bar{S}$, of the heavy isotope within a sphere is

$$\bar{S} = \left\langle 1 - \left\{ \frac{\operatorname{erf} \frac{a}{\sqrt{kDt}} + \frac{2}{\sqrt{\pi}} \left( \frac{\sqrt{kDt}}{a} \right)^3 \left( 1 - e^{-\frac{a^2}{kDt}} \right) - \frac{\sqrt{kDt}}{a\sqrt{\pi}} \left( 3 - e^{-\frac{a^2}{kDt}} \right)}{\operatorname{erf} \frac{a}{\sqrt{Dt}} + \frac{2}{\sqrt{\pi}} \left( \frac{\sqrt{Dt}}{a} \right)^3 \left( 1 - e^{-\frac{a^2}{Dt}} \right) - \frac{\sqrt{Dt}}{a\sqrt{\pi}} \left( 3 - e^{-\frac{a^2}{Dt}} \right)} \right\} \right\rangle \cdot 10^2 \tag{5}$$

where $a$ is the radius of the hypothetical crystal, $D$ the diffusion coefficient, $t$ the

time, and $k$ is defined by equation (3). This equation can be used to obtain a reasonably good idea of the mean percent enrichment of the heavy isotopes of an element diffusing out of a crystal.

The mean percent enrichment, $\bar{S}$, in a hypothetical spherical crystal is affected by time, the diffusion coefficients, the size of the crystal, and the percentage difference in the masses of the isotopes. $\bar{S}$ as a function of $a/\sqrt{Dt}$ is plotted in

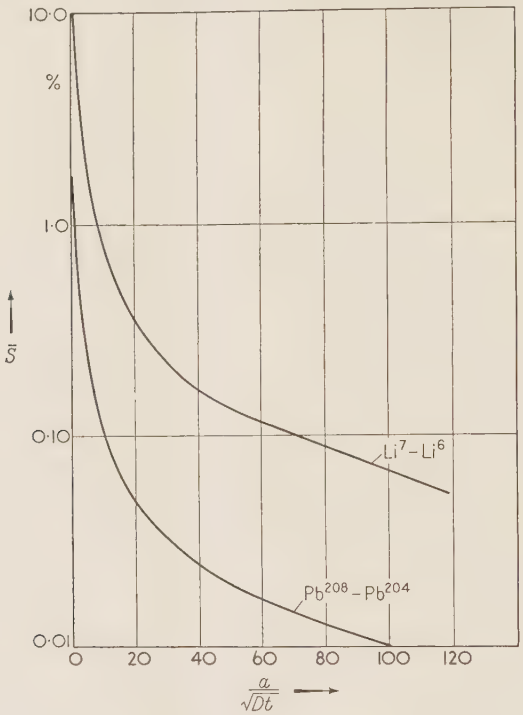


Fig. 2. Mean percent isotope enrichment as a function of the parameter $a/\sqrt{Dt}$ for lead and lithium.

Fig. 2 for the isotope sets of $Li^6$–$Li^7$ and $Pb^{204}$–$Pb^{208}$. Several percent change in isotopic abundance ratio is shown for the small values of $a/\sqrt{Dt}$, particularly in the light-mass range where the percentage difference in isotopic mass is greatest.

Qualitatively the relation is what one would expect. Given a diffusion path the average enrichment of the heavy isotopes in equal segments of the path will be greatest for those segments at the beginning of the path, and will increase inversely as the length of each segment. Hence, for small values of $a/\sqrt{Dt}$, that is, where $D$ and $t$ are relatively large and the radius of the crystal is small, a larger fraction of the atoms of a particular element will migrate from a crystal than if $a/\sqrt{Dt}$ were large. Consequently the enrichment of the heavy isotope will also be greater for small values of $a/\sqrt{Dt}$. Fig. 3 shows how rapidly the quantity, $Q$, of a given isotope remaining in the crystal decreases with increasing values of the mean percent enrichment of the heavy isotope.

Accepting, for the moment, solid-state diffusion as one of the replacement processes in natural crystals, to what extent would such a mechanism fractionate isotopes when considered in terms of practical values of $a$, $D$, and $t$? Fig. 4 shows

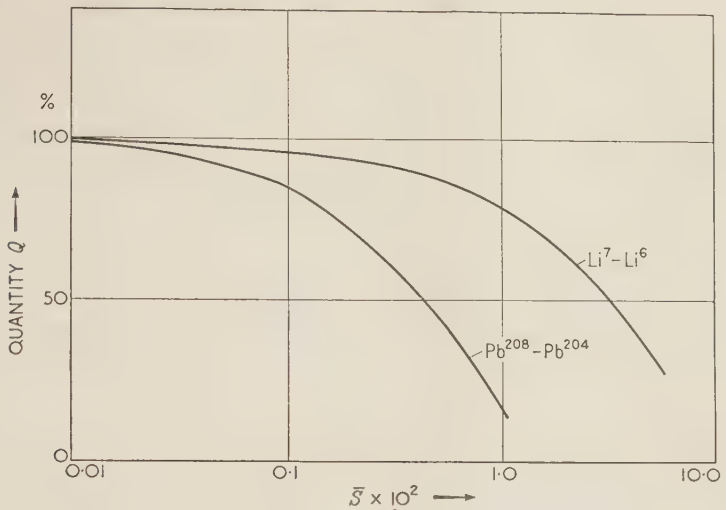


Fig. 3. Quantity of element removed as a function of the mean percent isotope enrichment for lead and lithium.

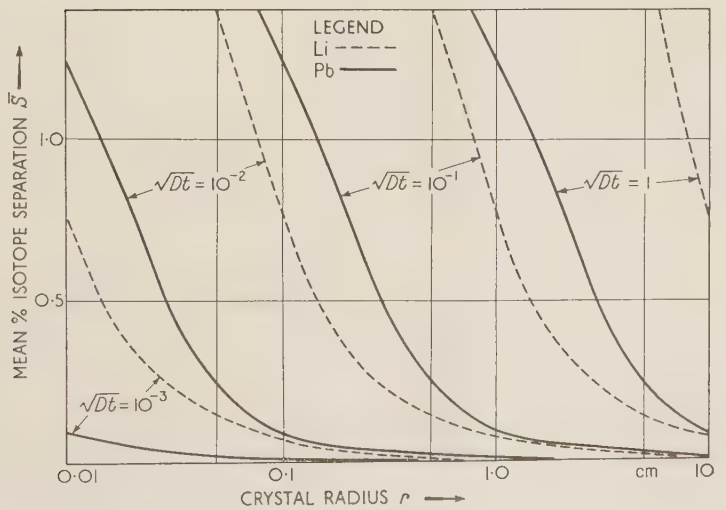


Fig. 4. Mean percent isotope enrichment, $\bar{S}$, as a function of crystal radius for lead and lithium for several values of $\sqrt{Dt}$.

a plot of the mean percent enrichment of the heavy isotope as a function of the radius "a" of a "spherical crystal" containing lithium and lead and for several values of the mean square path, $\sqrt{Dt}$. For values of $\sqrt{Dt}$ below $10^{-3}$ cm there

is no significant isotopic fractionation even in very small crystals, whereas above this value significant separation can occur, particularly in small crystals.

Data on solid-state diffusion coefficients in minerals at normal surface temperatures of the earth are scanty for most of the elements, but enough is known to indicate that the coefficients are extremely small in most cases. At these temperatures the diffusion coefficients for many elements are less than $10^{-22}$ cm$^2$/sec. For a typical old mineral of the earth, for example one a billion years old, $t$ will be about $3 \times 10^{16}$ seconds. For this value of $t$ and for the values of $D$ less than $10^{-22}$ cm$^2$/sec, the mean enrichment of the heavy isotope within a crystal due to solid-state diffusion must be of little importance at normal earth temperatures, even for crystals less than 0·10 cm. Some minerals are known to be considerably older than a billion years, and for such minerals isotopic fractionation due to diffusion could be significant for values of $D$ somewhat less than $10^{-22}$ cm$^2$/sec. However, where $D$ is large at these ordinary temperatures, significant fractionation may be possible even for diffusion time somewhat less than a billion years.

$D$ increases with temperature according to the general exponential law

$$D = D_0 e^{-\frac{A}{RT}} \tag{6}$$

where $D_0$ is the activation constant, $A$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. For minerals formed above 100°C and which have cooled slowly over a long period, the *average* diffusion coefficient could be as large as $10^{-16}$ cm$^2$/sec, depending on the temperature, whereas the diffusion coefficient at 20°C is much smaller. The diffusion time for rocks a billion years old being about $3 \times 10^{16}$ seconds, would thus make $\sqrt{Dt}$ equal to 1·7 cm and, of course, this could vary from this near maximum value all the way down to $10^{-7}$ cm or lower, depending on $t$. The large values of $\sqrt{Dt}$ plotted in Fig. 4 for lithium and lead show that under extremely favourable conditions of diffusion, that is, moderate to high temperatures and long periods of time, several percent change in isotopic abundance ratio could take place even in mineral grains as large as 1 or 2 cm in diameter. Frequently the value of the $\sqrt{Dt}$ is $10^{-3}$ and smaller; it is possible that, where $\sqrt{Dt}$ is greater than $10^{-3}$ cm, a change of the order of 0·5 to 1 or 2 per cent in the isotopic abundance could take place. This would be true especially where the percentage difference in mass is large, and where a sizable fraction of all the isotopes of a given element has diffused from the crystal.

To illustrate the above discussion, consider the diffusion of lead atoms in a galena lattice. At 27°C the diffusion coefficient for lead in lead sulphide is about $6{\cdot}1 \times 10^{-32}$ cm$^2$/sec (calculated from the data in Anderson and Richards, 1946), whereas at 460°C it is $4{\cdot}3 \times 10^{-13}$ cm$^2$/sec. Assume, for example, that the crystals of galena are a millimetre across and were formed under high-temperature (~500°C) conditions in a calcite matrix. After the cessation of crystal growth, diffusion of lead into the calcite lattice may become an important process. If the high-temperature conditions prevailed for 100,000 years, and assuming the diffusion coefficient of lead in calcite essentially the same as that in lead sulphide, then the

$\sqrt{Dt}$ would be 1·3 cm, which would be large enough to indicate an isotopic enrichment of the heavy isotope of several percent in the galena in this period of time. This is probably one of the less favourable examples of isotopic fractionation. Several other elements have much larger diffusion coefficients at high temperatures, and significant enrichment can take place in a much shorter time (1,000 to 10,000 years).

If one considers a high-temperature magmatic body such as a sill or dike which cools slowly over a minimum period of about one hundred years to a relatively low temperature, another possibility for significant isotopic solid-state diffusion arises. The crystals formed during the early stages of magmatic differentiation may undergo high-temperature replacement, as represented in Bowen's reaction series. For example, if a calcic plagioclase crystallizes first and continues to react with enclosing liquid magma forming more and more sodic feldspars, the end-product might be albite. Assuming that the calcium was replaced by sodium because of a variation in the ion concentration of the fluid magma with subsequent diffusion, substantial isotope separation might take place effectively in the small amount of original calcium remaining in the sodium feldspar crystal lattice. Under these temperature conditions the diffusion coefficients may be as large as $10^{-12}$ cm$^2$/sec or higher. In one hundred years ($t = 10^9$ sec) the $\sqrt{Dt}$ would be about $10^{-2}$ cm. From Fig. 4 it is seen that about 1 per cent change may take place in this relatively short time, even if essentially no diffusion took place from that time until the present.

Although significant isotopic separation can take place under these conditions, fractionation will only be evident in some minor-element constituent of a crystal, for example the heavy-isotope-enriched remnant of an element that was once present in large quantities. Thus assuming solid-state diffusion as the replacement process in the above example, a partly replaced plagioclase crystal, such as a calci-alkalic plagioclase, would not be expected to show significant enrichment of the heavy calcium isotopes, whereas trace quantities of almost completely replaced calcium in feldspar would probably exhibit some enrichment in the heavy isotopes.

*Isotopic fractionation across a boundary*

Replacement in the wall rock adjacent to a vein may take place by a diffusion process where a bodily flow of solution is impossible. This is true where initial vein solutions react with the wall rock forming an impermeable interface between the vein and the enclosing rock. Further penetration by the elements of the vein solutions into the wall rock and their replacement by certain constituents of that rock is not an uncommon process and is conceivably due to diffusion through the interface.

Where diffusion and replacement occur under high-temperature conditions a hydrothermal-alteration halo will be formed near the vein. The outer edges of this halo may be low-concentration diffusion fronts and as such may carry isotopes enriched in the lighter mass constituent. As the larger separation factors occur in the lower concentration areas at some distance from the contact, it is appropriate to determine the average isotopic separation beyond the outer edge

of the halo rather than the average for the whole halo. The usual equation for infinite diffusion across a boundary is

$$C_x = \frac{C_0}{2}\left(1 - \operatorname{erf}\frac{x}{2\sqrt{Dt}}\right) \tag{7}$$

where $C_0$ is the initial concentration and $C_x$ is the concentration at the distance $x$ from the interface. From this, Klemm (1943) has developed the equation

$$N = C_0\sqrt{\frac{Dt}{\pi}}\left\{e - \left(\frac{x}{2\sqrt{Dt}}\right)^2 - \frac{x}{2}\sqrt{\frac{\pi}{Dt}}\left(1 - \operatorname{erf}\frac{x}{2\sqrt{Dt}}\right)\right\}$$

$$= C_0\sqrt{\frac{Dt}{\pi}}\,\varphi\left(\frac{x}{2\sqrt{Dt}}\right) \tag{8}$$

where $N$ is the amount of material that has diffused in time $t$ through a 1 cm² area situated $x$ cm from the interface. By letting $\sqrt{k} = \sqrt{D_L}/\sqrt{D_H}$ where $L$ and $H$ have the previous meaning, then

$$\frac{N_L}{N_H} = \frac{\sqrt{k}C_{L_0}}{C_{H_0}} \cdot \frac{\varphi\left(\dfrac{x}{2\sqrt{D_L t}}\right)}{\varphi\left(\dfrac{x}{2}\sqrt{\dfrac{k}{D_L t}}\right)}$$

and

$$\bar{S} = \frac{\sqrt{k}\varphi\left(\dfrac{x}{2\sqrt{D_L t}}\right)}{\varphi\left(\dfrac{x}{2}\sqrt{\dfrac{k}{D_L t}}\right)} \tag{9}$$

where $\bar{S}$ is the mean enrichment of the light isotope in the atoms or ions that have diffused beyond a point $x$ cm from the interface. Klemm (1943) calculates $\bar{S}$ by means of two simple graphs (Figs. 5 and 6). Fig. 5 is the fractional amount of original material that has diffused beyond $x$ cm as a function of $x/2\sqrt{Dt}$ for various values of the mean square distance. Fig. 6 shows a plot of the mean percent enrichment $(\bar{S} - 1) \cdot 10^2$ as a function of $x/2\sqrt{Dt}$ for various percentage mass differences $\Delta m/m \cdot 10^2$.

As an example, let us consider the diffusion of lead in microperthite. At ordinary temperatures the diffusion effect of lead will be small even over geologic periods, but at high temperatures it could be significant in relatively short time. The approximate diffusion coefficient of lead in microperthite at 750°C is given by Rosenqvist (1949) as about $7{\cdot}5 \times 10^{-11}$ cm²/sec. If a lead-bearing ore is in contact with microperthite at 750°C for a period of a little more than four years (about $1{\cdot}3 \times 10^8$ sec), the value of $\sqrt{Dt}$ will be approximately 0·1 cm. If we now wish to consider a point $x$ cm from the contact such that the relative amount of lead, $N/C_0$, which has diffused beyond $x$ cm is 0·01, $x/2\sqrt{Dt}$ will be 0·75 (Fig. 5).

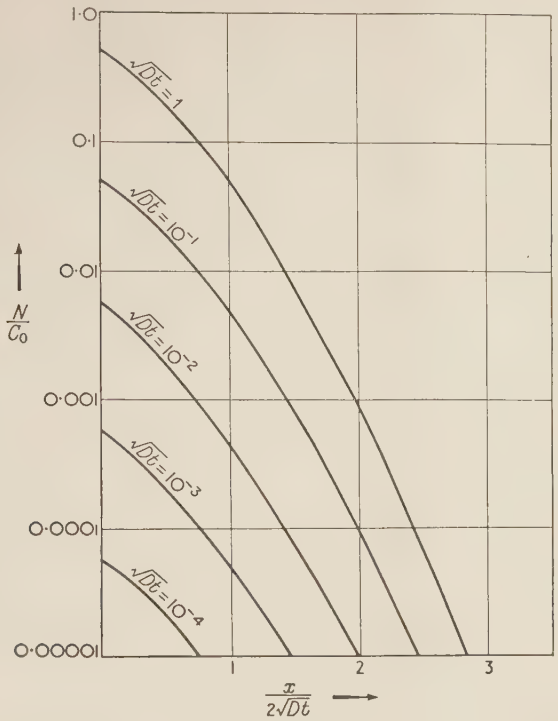


Fig. 5. Fractional amount of original material, $N/C_0$, which has diffused beyond $x$ cm as a function of $x/2\sqrt{Dt}$ for various values of $\sqrt{Dt}$ (after KLEMM).

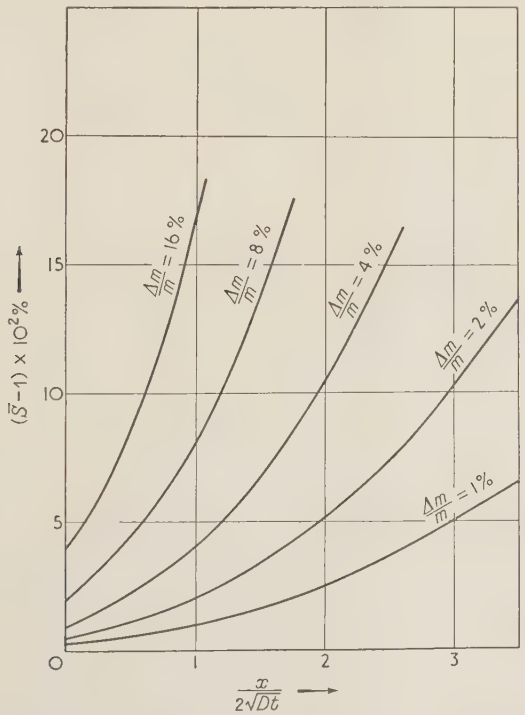


Fig. 6. Mean per cent enrichment, $(\bar{S}-1)\,.\,10^2$, as a function of $x/2\sqrt{Dt}$ for various percentage mass difference, $\Delta m/m\,.\,10^2$ (after KLEMM).

The percentage mass difference for $Pb^{204}$ and $Pb^{208}$ is 1·92 per cent, and hence from Fig. 6 the mean percent enrichment of $Pb^{204}$ in the lead that has diffused beyond $x$ cm will be about 1·5 per cent. If the diffusion had taken place for a little more than forty years instead of four years, then the same fraction of the original lead would show about 3 per cent enrichment in the light isotope. Isotopes of those elements with larger percentage mass differences will of course show larger enrichment factors. However, such an enrichment of the light isotope will be evident in only a very small fraction of the total lead that has diffused. Thus, the situation for diffusion across a boundary is similar to that considered for a crystal. For very small values of $\sqrt{Dt}$, say less than $10^{-3}$ cm, the amount of material exhibiting a large fractionation becomes vanishingly small. It is only where the $\sqrt{Dt}$ becomes greater than 0·1 cm that a significant fractionation takes place at such a distance where it may easily be recovered for isotopic analysis, and then for only a small fraction of the diffusing isotopes. For instance, in the four-year and forty-year diffusion examples the value of $x$ would be 0·15 cm and 2·90 cm, respectively, for 0·01 of the total number of diffusing lead atoms. In other words, one would expect to find significant isotopic fractionation due to this mechanism, but it would be very sharply localized and in a minor amount of material.

## Diffusion of Solutes

Up to this point we have considered the effect of solid-state diffusion only. However, once an atom diffuses from a solid lattice into an aqueous solution, such as ground-water solutions, it is free to move at much faster rates under similar concentration gradients. Solute diffusion—diffusion in an aqueous medium—is probably a much more important geologic process than solid-state diffusion, although both types of diffusion are usually concurrent. It is probable that in nature the wall rocks retain intergranular surface-water films and are permeable to and react with the hydrothermal solutions. Moreover, many rocks, such as limestones and dolomites, are porous and contain many cracks and channels. Under these conditions and where there is no fluid flow, solute atoms are free to travel through the intergranular water paths by diffusion. The same general laws apply as in solid-state diffusion; the really significant difference is that the solute diffusion coefficients are much larger. Thus, instead of considering a short-distance transfer one can expect a travel distance of several feet. For example, Morris and Lovering (1952) have studied the heavy-metal distribution in wall rocks of the Tintic district, Utah, and have shown that the distribution in wall rocks is indeed one that strongly suggests solute diffusion. These results indicate that both nonsteady-state (nonequilibrium) and steady-state (equilibrium) conditions existed, depending on the circumstances.

The results of nonsteady-state conditions will be similar to those shown for solid-state diffusion, except that the distances of diffusion will be longer for a given diffusion time due to the larger diffusion coefficients. For example, the solute diffusion coefficients in pure water for 1/2 $Zn^{++}$, 1/2 $Cu^{++}$, and 1/2 $Pb^{++}$ at 25°C are $7{\cdot}3 \times 10^{-6}$, $7{\cdot}4 \times 10^{-6}$, and $9{\cdot}7 \times 10^{-6}$ $cm^2/sec$, respectively. An aqueous solution containing zinc ion and flowing in a fissure vein may provide the

setting for the fractionation of $Zn^{64}$ and $Zn^{68}$. Assuming a steady supply of zinc ion at the vein wall, it can be shown that significant fractionation can take place in the zinc held by the interstitial fluid at such distances where the concentration is only 0·1 the concentration in the ore vein.

Consider the example of steady-state solute diffusion between two parallel veins. Garrels *et al.* (1949) have shown that such conditions can exist in water-saturated rocks where the diffusion front meets a vein in which pure water is flowing. The zinc removed by the water causes a front of near-zero concentration. Succeeding concentration fronts gradually "catch up" and steady-state conditions rapidly develop. Under steady-state conditions the amount of material, $dq$, deposited per area, $A$ cm², in time, $dt$, into the flowing water will be

$$dq = \frac{DA(C_0 - C_x)\,dt}{x}$$

$$= \frac{DAC_0\,dt}{x} \text{ (for } C_x = 0) \tag{10}$$

where $D$ is the diffusion coefficient and $x$ the distance from the source vein. Assuming $C_0$ to be the same for each isotope, the ratio of light to heavy masses being deposited in the water-carrying vein will simply be

$$\frac{Q_L}{Q_H} = \frac{kD_H}{D_H} = \sqrt{\frac{M_H}{M_L}} \tag{11}$$

Thus, under steady-state conditions the isotope separation is simply a constant fraction of the original isotope abundance regardless of the source concentration, time, or length of the diffusion path. It is of interest to point out that under these conditions the percent isotope enrichment would be

$$S = (k - 1) \cdot 10^2$$

Moreover, not only would $k$ be the ratio of any two of the zinc isotopes at any front between the two veins,* but it is also the abundance ratio of these isotopes diffusing to the water-carrying vein. Geologically this is of interest, because if the light material is continually redeposited at a given point it will form a zinc mineral isotopically lighter than the zinc in the original vein.

## Discussion and Evidence of Isotopic Diffusion

Because there is geological evidence that diffusion plays a part in forming some rocks and minerals, diffusion must be examined as a possible mechanism of natural isotope fractionation. The results presented here indicate that, although substantial isotopic fractionation is possible, it can occur only in very small parts of the original material. It is thus highly improbable that a large body exists in which a major constituent is isotopically enriched by diffusion processes; in

* In nature $C_0$ will not be the same for any two isotopes, and the ratio at any front will be $kQ_{H_0}/Q_{L_0}$ where $Q_{L_0}/Q_{H_0}$ is the original abundance ratio.

other words, significant isotopic fractionation will be localized and can be expected to be most apparent in minor elements of a given crystal or mineral. However, it is possible that an enrichment in the lighter isotopes of a major element might take place in replacement bodies formed by elements that have moved by diffusion of solute in magmatic solutions or in water-saturated rocks. As Garrels *et al.* (1949) have pointed out, solute diffusion reaches steady-state conditions in a relatively short time, and it has been shown here that under such conditions the enrichment factor will be $k$, or $\sqrt{M_H/M_L}$. Where steady-state conditions are not attained, the separation will be somewhat less than $k$. Thus a zinc mineral being formed by diffusion-transported zinc ions in solution would be expected to exhibit an enrichment in the light isotope by a factor of $k$ for steady-state condition, or some value less than $k$ for a nonsteady-state condition.

The salient feature of solute diffusion, as opposed to solid-state diffusion as a geologic process, is that more material can be moved faster over longer distances in relatively shorter times. Thus the elemental distribution, and hence isotopic abundance, in some rocks formed from diffusion-transported material will be influenced by solute diffusion. This assumes, of course, that the fractionation due to other processes that might produce isotopic separation will be comparable to or smaller than diffusion processes.

The foregoing discussion assumes that other natural processes have not interfered with the diffusion mechanism. Certain reactions can take place which will tend to equalize the theoretical isotope fractionation effect due to diffusion. For instance one must keep in mind that for ions transported by liquid diffusion there is always the possibility of chemical reaction and also that the ions are usually in a hydrated state. Any mechanism which will fix or change the migration velocity of the ions may tend to mask the fractionation effects.

The evidence for isotopic fractionation due to diffusion in natural material is very scanty, but it is worth while to examine some of the existing data. Probably the most direct evidence of isotopic diffusion so far found is the data determined by Silverman (1951) for $O^{18}$ and $O^{16}$. Across a contact of gabbro and intruding granophyre he made $O^{18}/O^{16}$ measurements of six specimens laterally spread over twenty feet. His results are shown in Table 1. The regular change of total oxygen and of the $O^{18}/O^{16}$ ratio might suggest a diffusion process. Silverman discusses a number of other possible processes in the light of geological evidence in the formations from which the specimens were taken. He finally concludes that his results indicate some process of permeation, solution, or diffusion in a solid. However, there is some doubt as to whether or not the above situation is one of solid-state diffusion. To explain diffusion transport over twenty feet the diffusion constants would have to be very large, implying a very high temperature, and it seems more probable that, if diffusion is the process, solute diffusion might be the mechanism.

There are a number of other examples where experimental data point to diffusion as a mechanism of natural isotope enrichment, but as yet no definitive experiments have been performed. It appears probable that concentration of isotopes by natural diffusion processes is a distinct possibility, and should be investigated further.

## Conclusion

Under certain favourable conditions at least part of the isotopic fractionation in natural specimens that has taken place during geologic time might be ascribed to a diffusion process. These processes, whether by solid-state or by solute diffusion, can produce significant fractionation up to a few percent in trace elements, but minerals grown over a period of time by small increments of an enriched trace element could display a bulk enrichment in the whole mineral crystal. To date, fractionation due to chemical differences has been favoured as an explanation, but it is the opinion of the authors that both mechanisms are operating, the particular circumstances controlling the importance of each mechanism in a given situation. Actually, experimental data must ultimately decide the issue.

The authors wish to thank R. M. Garrels of the U.S. Geological Survey and G. Wasserburg of the University of Chicago for their interest in this work and their helpful criticism. This work is part of a programme conducted by the Geological Survey on behalf of the Division of Research of the Atomic Energy Commission.

*Table* 1. *Variation of the* $O^{18}/O^{16}$ *ratio with concentration (after* Silverman, 1951)

| *Sample and number* | $O^{18}/O^{16}$(‰) | *cc* $O_2$/*mg sample* |
|---|---|---|
| Gabbro No. W-187 | 6·1 | 0·28 |
| Intermediate rock No. W-137-4 | 7·7 | 0·33 |
| Intermediate rock No. W-137-3 | 8·4 | 0·35 |
| Contact rock No. W-137-2 | 8·7 | 0·36 |
| Granophyre No. W-137-1 | 9·0 | 0·39 |
| Granophyre No. W-136-4 | 9·9 | 0·36 |

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# Composition and origin of basaltic magma of the Hawaiian Islands*

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ABSTRACT

Silica-saturated basaltic magma is the source of the voluminous lava flows, erupted frequently and rapidly in the primitive shield-building stage of activity, that form the bulk of each Hawaiian volcano. This magma may be available in batches that differ slightly in free silica content from batch to batch both at the same and at different volcanoes; differentiation by fractionation of olivine does not occur within this primitive magma. Silica-deficient basaltic magma, enriched in alkali, is the source of commonly porphyritic lava flows erupted less frequently and in relatively negligible volume during a declining and decadent stage of activity at some Hawaiian volcanoes. Differentiation by fractionation of olivine, plagioclase, and augite is evident among these lavas, but does not account for the silica deficiency or the alkali enrichment.

Most of the data of Hawaiian volcanism and petrology can be explained by a hypothesis that batches of magma are melted from crystalline peridotite by a recurrent process (distortion of the equatorial bulge by forced and free nutational stresses) that accomplishes the melting only of the plagioclase and pyroxene component but not the excess olivine and more refractory components within a zone of fixed and limited depth. Eruption exhausts the supply of meltable magma under a given locality and, in the absence of more violent melting processes, leaves a stratum of crystalline refractory components.

## I. Introduction

Current writing on basaltic magma in general and Hawaiian basalts in particular does not take full advantage of the wealth of published data in its treatment of the composition of the lavas and of the eruptive behaviour of Hawaiian volcanoes. This paper examines in detail the probable composition of Hawaiian magma, and presents a hypothetical process of origin and eruption that appears to fit the present knowledge of primary Hawaiian volcanic activity.

No new data are presented here. The factual material is drawn from the literature, and the ideas from many discussions with colleagues during my twenty years' interest in Hawaiian volcanoes. I particularly appreciate background discussions with the late T. A. Jaggar, with Ruy H. Finch, Gordon A. Macdonald, Austin E. Jones, Chester K. Wentworth, and Horace Winchell; I have profited greatly from constructive criticism by G. D. Robinson, Olcott Gates, Ray E. Wilcox, L. R. Wager, J. R. Balsley, and Earl Ingerson.

## II. Aspects of the Geology of Hawaii

The Hawaiian Islands are volcanoes piled on the ocean floor, forming a line beginning west of Midway Island and extending to the Island of Hawaii. Major volcanic activity has in general become extinct progressively from west to east; the two most active volcanoes today are the most southeasterly in the chain. All Hawaiian volcanoes in which structure is exposed are built largely or entirely of countless thin sheets of basaltic lava produced by frequent and voluminous eruptions during a primitive shield-building stage of activity. The two most active volcanoes, Kilauea and Mauna Loa, are considered to be still in this primitive stage. This shield-building lava is charged with volatiles, but its fluidity is such that insignificant amounts of pyroclastic deposits are formed at the vents. The great bulk of the lava produced in this stage is olivine basalt containing more than 5 per cent of modal olivine (mostly relict crystals not in equilibrium with the ground mass), about equal parts of labradorite feldspar and pyroxene and occasionally phenocrysts of hypersthene. Macdonald's useful definitions (1949b, p. 1544) are followed in this paper; thus *olivine basalt* contains 5 to 15 per cent of modal olivine, *basalt* contains less than 5 per cent of modal olivine, and *picrite basalt* contains 15 to 50 per cent of modal olivine. Only a few lava flows of picrite

basalt occur with the abundant olivine basalts, and the number of basalt flows in the primitive series is slightly more than the picrite basalts. Aside from the presence or absence of hypersthene, the rocks of this primitive stage differ mineralogically from each other, within the same volcano and between different volcanoes, largely in the amount of olivine present.

The upper part of the primitive shield of many of the volcanoes has characteristics that suggest a decline in the vigour of eruption. Some lava flows are separated by thin beds of ash and, in places, a little soil; pyroclastic eruption had apparently become more important and the time between eruptions had increased compared with the preceding stage of vigorous activity. The mineralogy also changed a little in the upper lavas; plagioclase phenocrysts are much more abundant, and augite phenocrysts which are absent from rocks of the bulk of the primitive shields are now found. Hualalai is considered to be in the declining phase of primitive shield-building (Macdonald, 1949a, p. 89).

This paper is concerned mostly with the primitive shield-building stage and the declining phase, because these dominant types of activity and their products must be most closely related to primary Hawaiian magma. To complete the sketch of the geology, however, the final stages of the Hawaiian volcanic life cycle are mentioned. The stagnation of activity and changes in mineralogy that characterize the decline of vigorous shield-building become more pronounced and even dominant in the last decadent stage of activity of several of the volcanoes. Mauna Kea, Haleakala, Kohala, and others are capped with a superstructure of large cinder cones and lava flows that show a variety of types ranging from picrites rich in both augite and olivine phenocrysts through oligoclase andesite to soda trachyte. Even nephelite-melilite basalts are found on Kauai and Koolau. Many of these later flows occupy deep erosional valleys, and soil horizons are almost universally present between flows, showing that long periods of quiet intervened between eruptions. It is important to realize that the total volume of these last-stage rocks is comparatively insignificant in the makeup of the whole volcano.

## III. Chemical Composition of Primary Hawaiian Magma

The magma that formed the lavas of the primitive shields of each Hawaiian volcano had a chemical composition that "approximates olivine basalt" (Macdonald, 1949b, p. 1567). Ample data are available, however, to make possible the separation of this generalization into several more precise concepts.

The fact that is lost in this generalization is that the abundant primary Hawaiian "olivine basalt" magma is not silica-deficient, as might be expected from its name, but is normally saturated with silica. The name "olivine basalt" should not be applied to the magma, since the name suggests a magma undersaturated in silica. Only small amounts of basalt magma deficient in silica are formed and they become available only during the decline of activity.

A deduction, obscured in Macdonald's generalization, is that all Hawaiian primary lavas may not have come from a common magma. Correlation in detail of the chemical and geological data suggests that Kilauea's historic lavas came from one batch of magma, Mauna Loa's historic lavas came from a different batch,

and prehistoric lavas of both these and the other Hawaiian primitive shields came from many different batches of magma. These supposed batches differ slightly from each other in chemical composition, particularly in silica content. Lavas from the two historic batches show some variation in chemical composition among themselves, which can all be accounted for by the differential movement of olivine phenocrysts during eruption of lava from each batch. But the difference in silica content between batches cannot be as readily explained by movement of olivine or hypersthene phenocrysts.

1. *Degree of silica saturation*

Olivine basalt, containing 5 to 15 per cent of modal olivine, makes up nearly two-thirds of the bulk of the lavas of the Hawaiian primitive shields. Twenty-four of the first-class chemical analyses represent olivine basalts that are known from field relations to belong to the primitive stage of eruption (see Appendix A). Of these twenty-four olivine basalts, eighteen are approximately saturated, showing less than 3 per cent of computed deficiency or excess of silica, and six of them show more than 4 per cent of excess silica; none has a silica deficiency greater than 3 per cent. Many olivine crystals are embayed and most of them must be considered relict crystals, not in equilibrium with their containing liquid, that have been preserved by quenching of the liquid at the time of extrusion.

Olivine basalt also is a product of the declining phase of the shield-building eruptions, and even the stages of senility. The volume of this rock in these associations is insignificant compared with that in the primitive shields. However, they commonly are the surface lava flow and commonly are less weathered than the rock of the older primitive shields; consequently they are represented among Hawaiian analyses greatly out of proportion to their importance in volume. It should be noted that these later-phase olivine basalts are characteristically undersaturated in silica (Fig. 1).

The concept that the parent Hawaiian magma was undersaturated must be due in part to the great number of analyses of these undersaturated rocks that are relatively so unimportant in volume. The concept is not justified; the composition of the olivine basalts in the primitive shields indicates that the primary Hawaiian magma is approximately saturated with silica, and it should not be called an olivine-basalt magma (see Tilley, 1950, p. 40).

2. *Batches of magma*

(a) *Definition by means of a special type of variation diagram*—Diagrams showing the chemical variation among the analyzed lavas of the Hawaiian primitive shields bring out patterns of variation that can best be explained by the assumption that suites of closely related rocks were produced from batches of magma that were generally basaltic but that differed from each other significantly in their original silica content. These differences may be shown by means of a variation diagram which shows content of magnesia rather than silica as abscissa, inasmuch as the biggest known difference between these lavas is in their content of magnesia-rich olivine. The small but significant variations of silica are more easily seen in this type of plot. Total silica, total iron (includes FeO, 0·9 of $Fe_2O_3$, and MnO),

lime, and total alkali are plotted as ordinate values. Analyses were not recalculated as water-free; to do so would not change the relative position on the plots, and it would appreciably change only silica on the scale of the plot, because water is consistent and much less than 1 per cent in all analyses. Fig. 2 illustrates the method with a small number of analyses. Four analyses of Hawaiian olivine phenocrysts (Aurousseau and Merwin, 1928, p. 560) are plotted, and lines from this plot are extended into the diagram and labelled "olivine control" because they indicate the straight-line variation that would result from changing the

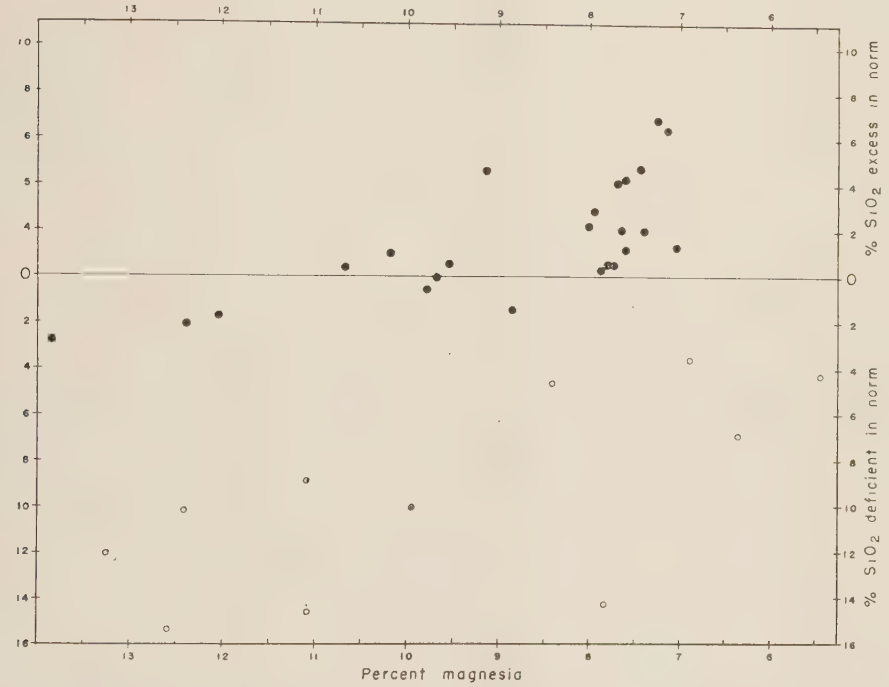


Fig. 1. Silica saturation of olivine basalts (containing 5–15 per cent of modal olivine) of Hawaii. Solid circles represent the abundant lava of the primitive shields, open circles, the relatively scarce lava of the declining activity. The ordinate represents excess or deficiency of silica after computing normative feldspar, pyroxene, apatite, and iron ores.

amount of olivine in any plotted rock composition through which the lines are drawn. The composition of the olivine phenocrysts is nearly constant in this group of lavas (the magnesia content of the olivine phenocrysts ranges from about 47·5 to 48·5 per cent, and silica from about 40·3 to 40·9 per cent), so for simplicity I have used the average composition as fixed points from which to draw the olivine control spokes. Comparable "hypersthene control" lines were fixed by plotting the composition of a Bonin Island phenocryst containing about $En_{85}$ (Kuno, 1954, Pt. 2, p. 34), since no hypersthene phenocrysts from Hawaiian basalts have been analyzed.

(b) *Historic batch of magma at Kilauea*—Fifteen first-rate analyses of Kilauean lavas erupted between 1840 and 1929 are represented on Figs. 2 and 3. Eleven of the silica values plot within 0·25 per cent of an "olivine control" line; the

greatest departure is less than 0·5 per cent. Plots of iron, lime, and alkali show greater departure from the appropriate olivine control lines, but the departures are erratic and not systematic. This straight-line variation of silica with respect to magnesia confirms the mineralogical observation that these lavas differ largely in their content of olivine. The somewhat erratic variation of iron, lime, and alkali with respect to magnesia suggests that there is some variation in the content

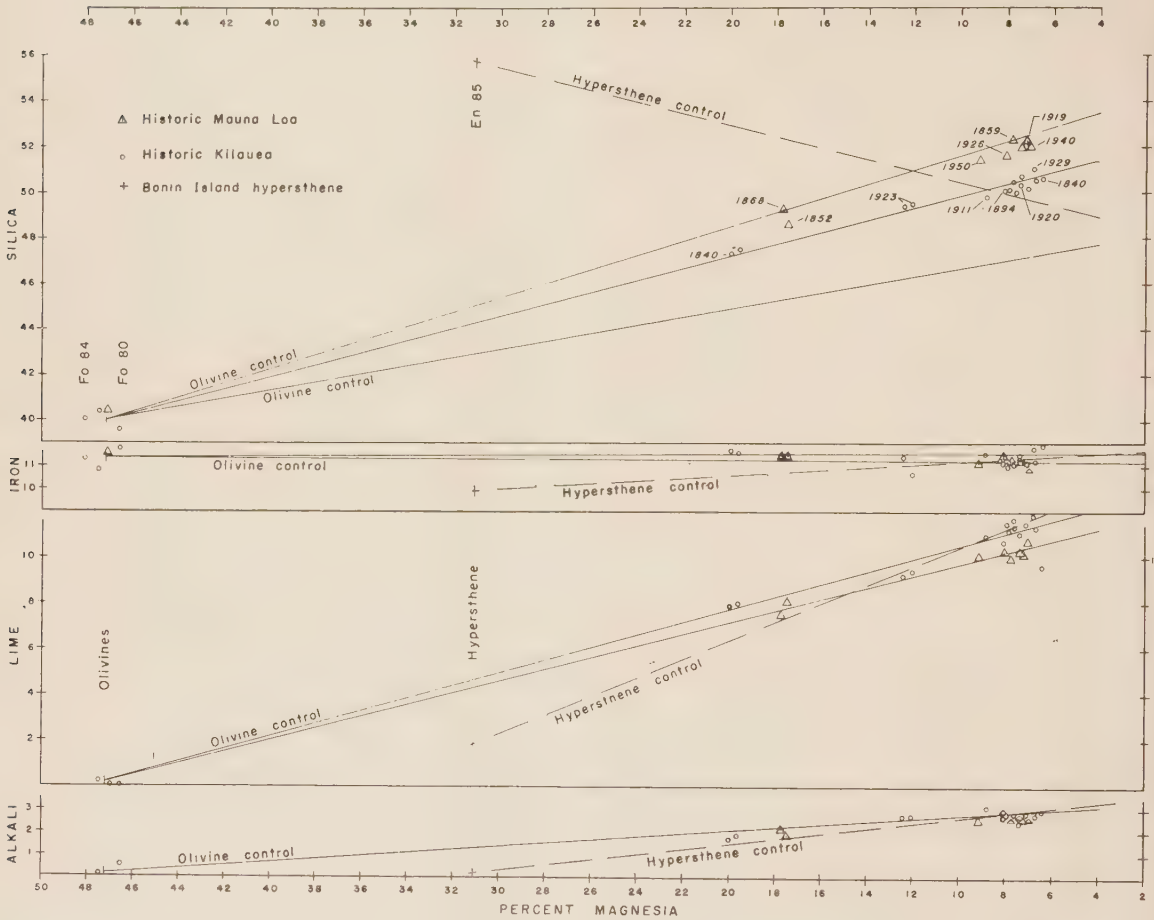


Fig. 2. Variation of weight per cent of silica, iron (FeO + 0·9 $Fe_2O_3$ + MnO), lime, and alkali ($Na_2O + K_2O$) with weight percent of magnesia in representative chemical analyses of lavas and their olivine phenocrysts erupted in historic activity of Kilauea and Mauna Loa, Hawaii. Control lines from olivine (and hypersthene) indicate the linear change in oxide constituents producible by increasing or decreasing the amount of olivine (or hypersthene) in magmas of different composition. A few iron and alkali points are omitted due to crowding on the graph.

of magnetite and plagioclase that is not controlled by the addition or subtraction of olivine crystals. Granting a slight heterogeneity in distribution of magnetite and plagioclase, at least among the pieces used for chemical analysis, the historic lavas of Kilauea could all have been derived by movement of olivine phenocrysts into or out of a single liquid magma whose silica content was about 50 per cent.

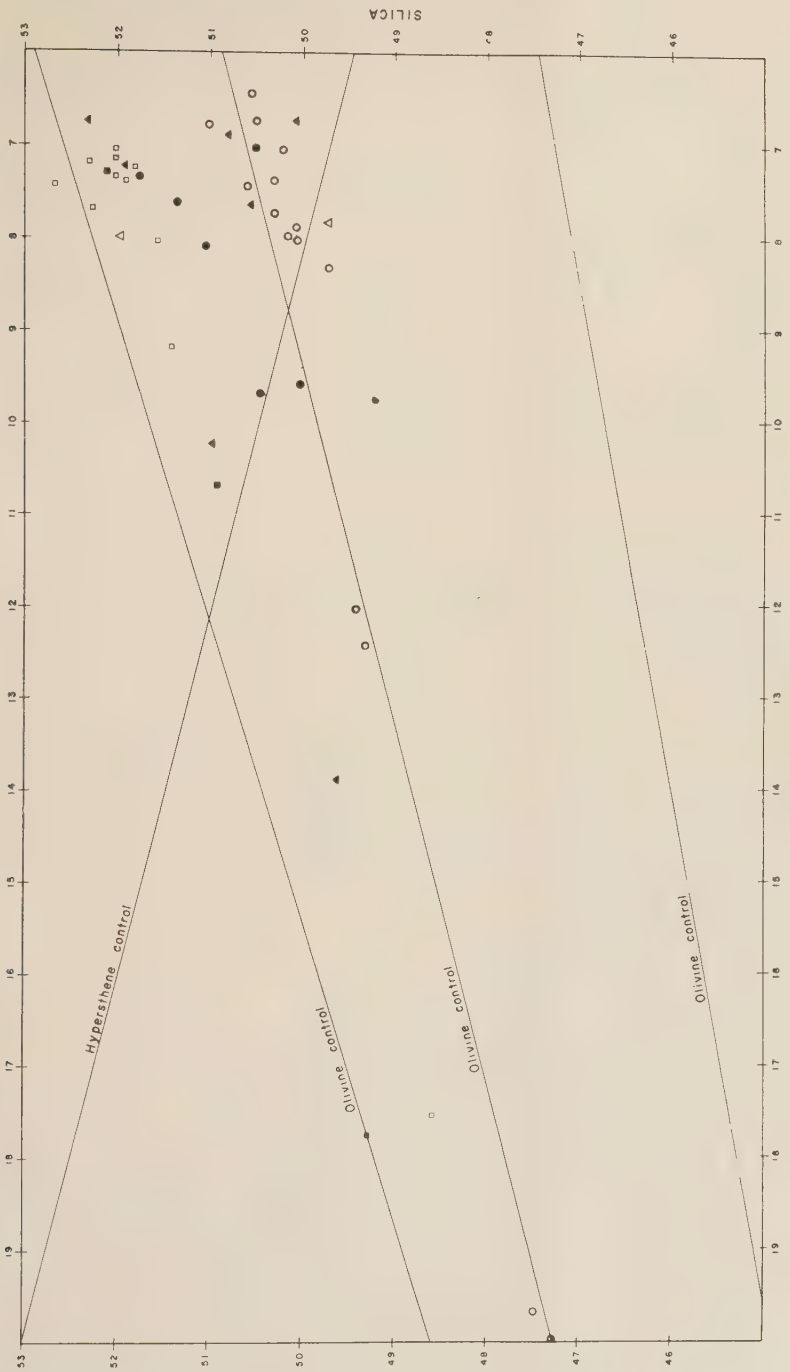


Fig. 3. Enlargement of part of Fig. 2, showing variation of silica with magnesia in all first-rate analyses of picrite basalt, olivine basalt, and basalt erupted in the primitive shield-building stage of activity of several volcanoes of Hawaii. Open circles, Kilauea historic; solid circles, Kilauea prehistoric; open squares, Mauna Loa historic; solid squares, Mauna Loa prehistoric; open triangles, Kohala; solid triangles, Koolau.

(c) *Historic batch of magma at Mauna Loa*—Eight analyses of Mauna Loa lavas ranging in date of eruption from 1852 to 1950 are less well-distributed along the abscissa on Fig. 2. (Twelve are plotted on Fig. 3.) They are all higher in silica and lower in lime than the Kilauea analyses, but all plot near a different olivine control line. The historic Mauna Loa lavas are all nearly 2 per cent richer in silica than the lavas of Kilauea.

(d) *Prehistoric batches of magma*—Six analyses of prehistoric lavas of Kilauea and three from Mauna Loa show erratic distribution with respect to the historic lava plots. Three of those from Kilauea could be from the historic Kilauea liquid, but three of them are too high in silica. Two of the prehistoric Mauna Loa lavas have silica comparable to that of the historic batch; one of them is much lower in silica.

Nine analyses of lava from the primitive shields of Koolau and Kohala likewise show erratic distribution in terms of a single olivine control line, but all plot essentially within the limits of variation exhibited by the historic lavas from Mauna Loa and Kilauea. All could be produced by moving olivine crystals into or out of liquids that differ from each other mostly in their content of excess silica.

(e) *Validity of data*—The silica differences plotted are so small, is one justified in giving them any significance? A brief scanning of the record shows that the differences cannot be charged to any pattern of field collecting or of analytical procedure. The specimens of Mauna Loa and Kilauea lavas were collected in the field by at least ten different men. The chemical analyses represent the work of ten different analysts, in five different laboratories, over a span of fifty years of changing techniques. The suite of thirteen historic Kilauea analyses that shows such a remarkable linear relation between silica and magnesia represents the field collections of six different men, and analytical work by nine different analysts at five different laboratories. It seems utterly improbable that the consistent differences plotted could be due to chance. The differences appear to me to be real, and a valid basis for speculation.

### 3. *Composition of batches of primary magma*

The clustering of analyses between $7\frac{1}{2}$ and 8 per cent of magnesia suggests that the batches of primary magma contained slightly more than 8 per cent of magnesia. In that interval on the abscissa, the silica content of magma batches ranges from about 50 per cent to 52 per cent. The rocks represented by the analyses in this part of the variation diagram, expressed in normative minerals, contain about 45 per cent each of labradorite plagioclase and pyroxene and about 10 per cent of accessory constituents. It is suggested that the batches of primary Hawaiian magma that yielded the shield-building lavas were composed essentially of equal parts of plagioclase and pyroxene, but differed slightly from each other in the amount of excess silica and accessory oxides.

Possible compositions of the historic magmas of Kilauea and Mauna Loa have been computed, weighting the available chemical analyses according to Macdonald's estimates of the distribution of rock types (quoted on page 88 among

the historic lavas of both volcanoes. The weighted average composition and the computed norm for each historic magma are tabulated below.

*Computed* chemical composition of historic magma of Kilauea and Mauna Loa*

| *Oxide wt. %* | *Kilauea* | *Mauna Loa* | *Computed norm* | *Kilauea* | *Mauna Loa* |
|---|---|---|---|---|---|
| $SiO_2$ | 50·08 | 51·76 | Qu | 0·36 | 5·34† |
| $Al_2O_3$ | 12·93 | 12·65 | or | 2·78 | 2·22 |
| $Fe_2O_3$ | 1·51 | 2·37† | ab | 18·34 | 18·34 |
| FeO | 9·95 | 8·88 | an | 23·91 | 23·91 |
| MgO | 8·66 | 8·50 | (fspar | 45·03 | 44·47) |
| CaO | 10·96 | 9·94 | wo | 11·95 | 9·86 |
| $Na_2O$ | 2·20 | 2·19 | fs | 12·80 | 9·24† |
| $K_2O$ | 0·50 | 0·38 | en | 21·60 | 21·30 |
| $P_2O_5$ | 0·29 | 0·26 | (pxene | 46·35 | 40·40†) |
| $TiO_2$ | 2·69 | 3·31 | mt | 2·09 | 3·48† |
| | | | il | 5·17 | 6·23 |

* Rock analyses weighted in average according to MACDONALD's estimate of proportions of olivine basalt, basalt, hypersthene-bearing basalt, and picrite among historic lavas of the two volcanoes.

† Higher ferric iron, due to secondary hematite in two of the analyzed specimens, increases Qu and mt and decreases fs in the theoretical mineral composition. In the rocks, pyroxene content is about the same in both suites.

4. *Possible explanation of silica differences*

The variation diagram, Fig. 2, shows that the differences in silica content between the Kilauea and Mauna Loa historic suites cannot have been produced by moving only olivine crystals into or out of a homogeneous common parent magma. The plotted points of the two suites cluster along different olivine control lines that are separated by nearly 2 per cent of silica at about 8 per cent magnesia. The plotted values also show not the slightest suggestion of grouping along a hypersthene control line for silica, thus giving little encouragement to the supposition that movement of hypersthene crystals alone may have played a significant part in the differentiation (POWERS, 1935, p. 67). However, inasmuch as the olivine and the hypersthene control lines for silica slope in opposite directions, it is theoretically possible to account for the silica-magnesia relationships between the different primitive shield magmas by moving both olivine and hypersthene into or out of a single parent magma. The results of some computations are shown in Appendix B that account for the silica and magnesia content of some analyzed Koolau lavas by fractional crystallization and migration of crystals of olivine and hypersthene. Special conditions modifying the operation of the process are stipulated where necessary to fit the theoretical results to field and petrographic data. If, for instance, an original magma with relatively high silica content is chosen, the sub-magmas generally require reheating at appropriate times; if an original magma with low content of silica is chosen, the process yields a large

amount of low-enstatite liquid at the top of the magma chamber that is not represented by surface flows and therefore was not erupted at all; both these conditions seem to me improbable. Thus I conclude that the process of fractional removal of olivine, or of hypersthene, or of both sorts of crystals, offers no help in accounting for the differences in silica between the historic lava suite of Mauna Loa and that of Kilauea, and likewise between the lava suites of other primitive shields. Parenthetic to this discussion, I should state that during the declining stages of activity at some Hawaiian volcanoes, differentiation by fractional crystallization appears to have been important, and evidence for this is presented below.

As an alternative process, migration of silica in a fluid within a single magma should be considered. The addition of secondary silica to old rocks in the vicinity of major vents is known in Hawaii (Macdonald, 1949a, p. 91), but the field evidence suggests that it is locally a possible but not a common process in Hawaiian volcanism. If it were accepted, in the face of contrary field evidence, as a process competent to explain the silica differences in question, why did it not function in the magma during historic Kilauea eruptions and produce erratic relationship between silica and magnesia in those lavas? No satisfactory reason is apparent.

If neither fractional crystallization nor migration of silica-rich fluid within a single magma seems competent to explain the silica differences, perhaps a reasonable explanation is that Hawaiian magma was not a single magma of uniform composition, but was produced in batches that differed originally in silica content. The writer concludes from the evidence offered by the chemical variation diagram that the historic lavas of Kilauea were derived from one batch of magma, those of Mauna Loa from a different batch, and that prehistoric lavas from these two and other primitive shields were derived from many other batches of magma. This concept is not in conflict with other evidence considered in following paragraphs.

## IV. Differentiation and Eruptive History of Batches of Primary Magma

Examination of the existing data shows that the magnesia content of the bulk of the lava does not change progressively throughout the postulated existence of a batch of magma, or throughout the major shield-building stage of any of the Hawaiian volcanoes. The differentiation that is found among these lavas is apparently due to erratic and short-lived episodes of settling of olivine crystals during eruption. Gravitative separation of phenocrysts from a source magma apparently does not take place in the intervals between actual eruption throughout the shield-building stage of activity.

### 1. *Koolau magma*

Erosion has exposed the lavas of the Koolau primitive shield volcano to a depth of at least 3,000 feet below the surface of the shield. Specimens of lava

from different depths within the structure have been analyzed, and the following tabulation shows that there has been no progressive reduction in magnesia content from oldest to youngest (data from WENTWORTH and WINCHELL, 1947, p. 67–71).

| *Depth in shield (feet)* | *Per cent magnesia in analysis* |
|---|---|
| 200 to 300 | 10·18 Hypersthene porphyritic basalt<br>7·21 Olivine basalt (using Macdonald's definition) |
| 1,000 | 13·86 Ol.-hyp. porphyritic basalt |
| 1,500 | 6·70 Olivine basalt |
| 2,500 | 7·64 Olivine basalt |
| 3,000 | 6·96 Hyp. porphyritic basalt<br>6·88 Olivine basalt |

2. *Mauna Loa magma*

The shield of Mauna Loa has not been greatly dissected by erosion, but it is generally accepted that part of an early stage of the shield is exposed in the Ninole volcanic series. MACDONALD has estimated the proportion of three lava types among the four volcanic series into which the Mauna Loa shield-lavas have been separated. I have rounded his figures to the nearest 5 per cent, and added my own estimate of the total abundance of each named series, in the following table:

| *Named volcanic series* | *Picrite basalt % of vol.* | *Ol. basalt % of vol.* | *Basalt % of vol.* | *No. analyses of basalt and ol. basalt, and range of MgO content* |
|---|---|---|---|---|
| Kau volcanic series historic, not 1 per cent of bulk of shield | 10 | 15 | 75 | 8 analyses<br>MgO range 8·02–7·15 |
| Kau volcanic series prehistoric, less than 10 per cent of shield bulk | 20 | 45 | 35 | 3 analyses<br>MgO range 7·68–5·90 |
| Kahuku volcanic series less than 20 per cent of shield bulk | 20 | 40 | 40 | No analyses |
| Ninole volcanic series about 70 per cent of shield bulk | 15 | 60 | 25 | 2 analyses<br>MgO range 9·80–7·10 |

The magnesia content of the analyzed lavas shows no progressive change from old to young lavas, though the amount of modal olivine present in the younger lavas has decreased, as evidenced by the increase in proportion of basalt at the expense of olivine basalt.

3. *Kilauea magma*

The approximate proportion of three lava types among the Kilauean lavas has been estimated by Macdonald (1949a, p. 57). The following table uses his data rounded to the nearest 5 per cent:

| *Named volcanic series* | *Picrite basalt % of vol.* | *Ol. basalt % of vol.* | *Basalt % of vol.* | *No. analyses of basalt and ol. basalt, and range of MgO content* |
|---|---|---|---|---|
| Puna volcanic series historic | 5 | 80 | 15 | 13 analyses MgO range 12·41–6·38 |
| Puna volcanic series prehistoric | 5 | 70 | 25 | 7 analyses MgO range 9·68–6·73 |
| Hilina volcanic series | 5 | 65 | 30 | No analyses |

Olivine basalt has been the dominant lava type, and the analyzed specimens of both olivine basalt and basalt show no cumulative change in magnesia content throughout the magmatic history of Kilauea. The following detailed examination of the record of historic activity confirms this generalization and suggests that the known movement of olivine crystals to produce both picrite and basalt as minor differentiates takes place unpredictably during a late phase of some eruptions.

4. *Historic changes and eruptive history at Kilauea*

The information available on the composition of the lavas erupted during twelve episodes of historic activity is outlined in the following table. The greatest difference in magnesia content is shown by two lavas that were erupted almost simultaneously in 1840, and no cumulative change in magnesia content during the century is suggested by the data.

The activity from 1913 to 1924 is best recorded. Starting from a short period of quiet without liquid lava visible in the crater in mid-1913, lava reappeared and re-established the "perpetual" molten lake in a series of minor fluctuations lasting through 1916. In 1917 the tempo of lava output increased, and eruption of more than 3,300 million cubic feet of olivine basalt produced filling and overflow from the crater between 1918 and 1921. Lava output then diminished to a series of fluctuations of the lake within the crater, and two small rift flows, one of basalt in 1922 and one of olivine-rich basalt in 1923, both of insignificant volume. This

episode of activity ceased with engulfment at the crater accompanied by the minor phreatic eruption in the spring of 1924.

Certainly there has been no progressive depletion in the magnesia content of Kilauea lavas during a hundred years of almost continuous activity. One is forced to conclude that conditions at the magma source did not permit fractional crystallization and removal of olivine phenocrysts during this entire time. One might even question the existence of a magma reservoir in the intervals between eruption, except that the chemical analyses of the Kilauea historic lavas indicate so strongly that all these lavas came from a melt of single composition.

*Historic eruption and differentiation at Kilauea*

| *Activity from* | *Ending in* | *Crater lava type* | *MgO (per cent)* | *Rift flow type* | *MgO (per cent)* |
|---|---|---|---|---|---|
| 1913–1924 | engulfment | ol. basalt (1) 1921 | 7·61 | ol. rich basalt (2) 1923 | 12·41–12·04 |
| | | ol. basalt (2) 1920 | 7·44–7·39 | basalt (2) 1922 | — |
| | | ol. basalt (1 and 2) 1919 | 7·96–7·03 | | |
| | | ol. basalt (1) 1917 | 7·89 | | |
| 1903–1913 | minor collapse | ol. basalt (3) 1911 | 8·83 | none | |
| 1894–1903 | | period of inactivity | | | |
| 1891–1894 | engulfment | ol. basalt (4) 1894 | 8·01 | none | |
| 1886–1891 | engulfment | ol. basalt (5) | | none | |
| 1879–1886 | engulfment | ol. basalt (6) | | none | |
| 1871–1879 | minor collapse | not collected | | basalt (2) 1877 | |
| 1868–1871 | | period of inactivity | | | |
| 1855–1868 | engulfment | not collected | | ol. basalt (2) 1868 | |
| 1849–1855 | minor collapse | not collected | | none | |
| 1840–1849 | minor collapse | ol. basalt (7) | | none | |
| 1832–1840 | engulfment | ol. basalt (8) | | picrite (9) 1840 | 19·96 |
| | | | | basalt (9) 1840 | 6·38 |
| 1823–1832 | engulfment | not collected | | basalt (2) 1832 | |
| ?–1823 | engulfment | not collected | | basalt (2) 1823 | |

(1) Macdonald and Eaton (in prep.), Table 9
(2) Macdonald, 1949a, p. 66.
(3) Macdonald, 1949a, p. 74.
(4) Phillips, A. H., 1894, p. 473
(5) Dana, E. S., 1889, p. 458–459.
(6) Silvestri, O., 1889, p. 132 and 140.
(7) Cohen, E., 1880, p. 29.
(8) Dana, J. D., 1879, p. 134
(9) Macdonald, 1949b, p. 1572.

Though there has been no apparent cumulative removal of olivine crystals from the source body of magma, there are a few lava flows whose compositions indicate concentration of and removal of olivine crystals. The two extreme differentiates of this sort were erupted almost simultaneously in 1840 (Macdonald, 1944). These two rift eruptions, and a tremendous engulfment in the caldera, culminated about three years of vigorous eruption which had completely refilled and overflowed the great crater formed during an even greater engulfment in 1832. Another pair of olivine-rich and olivine-poor differentiates were erupted

in 1922 and 1923 following four years of vigorous eruption that produced great volumes of only the common olivine basalt. Apparently the gravitative settling of olivine crystals is an erratic event that takes place unpredictably during periods of actual eruption and probably high in the column of magma that is feeding the surface eruption.

5. *Absence of dunite xenoliths in shield lavas*

The almost complete absence of xenoliths of dunite in the lavas of the primitive shields has significance in the discussion of differentiation among these lavas. No dunite xenoliths have been found in any lava from Kilauea. A few small ones were found in the 1950 lava-flow of Mauna Loa, and in one prehistoric flow located in the area of overlap between flows from Hualalai and Mauna Loa (that might not be a Mauna Loa flow). Dunite xenoliths are extremely rare or absent from the exposed primitive shields of all other Hawaiian volcanoes. This is in striking contrast to their abundance among lavas of the later phases of declining activity on some volcanoes. This almost complete absence of xenoliths or glomerocrysts of olivine rock among all the lava flows erupted during the primitive shield-building stage of activity seems to me to prove that no appreciable amount of crystalline olivine was present in, or even accessible to, the magmas that were the source of the primitive flows.

6. *Discussion of differentiation*

While it is apparent that olivine phenocrysts are almost universally present in the lavas of the Hawaiian primitive shields, it is equally apparent that there has been no progressive decrease in the magnesia content of the lavas, from old to young, of the three better-known primitive shields, nor in the historic lavas of Kilauea which cover a span of a hundred years. It is strongly suggested by the absence of dunite xenoliths that the original magmas contained no appreciable amounts of crystalline olivine. It must be concluded that there has been no cumulative gravitative movement of olivine crystals within such original magmas throughout the primitive shield-building stages of activity. There has been, however, gravitative movement of olivine crystals as erratic events associated with rise of magma to the surface.

Were conditions such that olivine, in the bodies of original magma, was not permitted to crystallize? Or were the crystals formed, but not permitted to settle in the magma? Were there, perhaps, no bodies of magmatic liquid between periods of actual eruption?

Let us first assume that the magma was melted from crystalline crustal material. Since the mafic silicate part of the lava is just saturated in silica, an increase in crustal temperature to accomplish the melting must have been sufficient to melt material of basaltic composition in the crust (including olivine that forms when the enstatite molecule is melted, expressing the reasoning in terms of the binary system forsterite–silica), but not enough to dissolve more refractory olivine present in equilibrium in the crust. If this temperature were maintained, the melt could retain this limited amount of potential olivine in the liquid, other conditions

remaining constant. Probably this necessarily delicate temperature balance could be maintained (somewhat above the normal crustal temperature) if the conditions that caused the melting were approximately maintained. In contrast, if comparable melting were caused by sudden release of pressure, as by rupture of the crust, the melt would begin to crystallize again as soon as normal pressure conditions were restored. If this were the action, olivine crystals would form but probably would not sink because the enclosing magma would be rigid and in the process of crystallizing. However, the eruptive history of Kilauea seems to require the existence of a body of readily eruptable magma, at least during the period of historic time. Kilauea, in all respects, appears to be so typical of Hawaiian primitive shield-building activity that it seems necessary to conclude that magma is maintained in a readily eruptible state during the life of a batch under physical conditions that do not permit the crystallization of olivine that is available in the $MgSiO_3$ part of the melt.

### 7. *Eruptive history and the concept of magma batches*

Waxing and waning of volcanic activity in periods of several hundred years' duration is apparent in the recent history of both Kilauea and Mauna Loa. Three periods of vigorous extrusion of lava, including the historic period, have been separated by periods of diminished activity characterized by caldera collapse and enlargement and by phreatic eruption. For several hundred years prior to 1790, phreatic eruptions and enlargement and deepening of the summit caldera characterized the activity at Kilauea (Powers, 1948, p. 291–292). This period of waning lava eruption was preceded by one of great lava extrusion which filled an older summit caldera and added effluent lava to its outer slope. A second period of waning activity (going backward in time) is indicated by deposits of pyroclastic material within the old caldera and on its outer slopes, which received no flooding by lava flows during a time-interval long enough for a forest to become established up to the caldera rim. The shield summit in which this old caldera developed was built by a still earlier (third) period of great lava extrusion.

The historic period of great activity of Mauna Loa was preceded by a time of relative inactivity during which the surfaces of the older flows were weathered to an appearance of antiquity in striking contrast to the freshness of surface of the historic and immediately prehistoric flows (Finch, 1923).

This waxing and waning of eruptive activity is not mentioned as proof of the development of Hawaiian magma in separate batches, but it is the eruptive behaviour which would be expected if magma were formed as a batch, extruded vigorously until exhausted, then another batch formed in the same place.

## V. Depth of Origin of Hawaiian Primary Magma

There are no data on which to base a precise estimate of the depth at which Hawaiian primary magma is formed. A suggestion that this depth may be of the order of magnitude of thirty to thirty-five miles may be taken from the fact that earthquakes originating near that depth have preceded eruption of lava at the surface. More and better data that are gradually being accumulated may prove

whether this suggested correlation between depth of earthquake origin and depth of magma origin has merit or is unjustified; the present data are, however, summarized. The general area of outbreak and the imminence of the April 1942 flank eruption of Mauna Loa was correctly predicted by appraisal of the seismic prelude to the eruption (FINCH, 1942). A swarm of earthquakes originating at depths approximating twenty-seven miles was recorded in December, 1941; another swarm was recorded in February, 1942, originating northeast of Mauna Loa at about thirty miles depth, followed by a sequence of quakes whose centres approached closer to the surface and migrated geographically along the major flank rift of Mauna Loa; this pattern enabled FINCH to make the prediction at the end of March that an outbreak from the northeast rift was imminent. The general area of outbreak of the June 1950 flank eruption of Mauna Loa was also correctly predicted (FINCH and MACDONALD, 1950) by appraisal of the seismic pattern, which, however, started at shallower depths. The possibility that the 1950 eruption started from shallow depth and that the magma remained high in the volcanic system between the eruptions of 1949 and 1950 is suggested by two other unrelated facts: the tilt pattern for this interval did not indicate contraction of the Mauna Loa structure (which had swelled somewhat prior to the 1949 eruption), and the lava of 1950 contained small dunite xenoliths which might represent accumulations of olivine phenocrysts during the interval between the two eruptions.

In contrast to these two successful predictions based on the seismic prelude, neither the points of outbreak nor the imminence of eruption was detected from contemporaneous study of the earthquakes occurring before the Mauna Loa summit eruptions of 1949, 1940, or 1933, nor before the Mauna Loa flank eruption

| *Earthquakes* | | *Eruption* | |
|---|---|---|---|
| *Location* | *Date* | *Place* | *Date* |
| Two, 33 and 35 miles deep | Feb. 1933 | Mauna Loa caldera | Dec. 1933 |
| Several, 27 miles deep | April–May 1934 | Kilauea caldera | Sept. 1934 |
| Two, 44 and 39 miles deep | Oct. 1934 | | |
| Several, 25–30 miles deep | Sept. 1935 | Mauna Loa flank | Nov. 1935 |
| Several, 35–40 miles deep | July–Aug. 1939 | Mauna Loa summit | April 1940 |
| Swarm, 27 miles | Dec. 1941 | | |
| Several, 30 miles | Feb. 1942 | Mauna Loa flank | April 1942 |
| Several, 30–40 miles deep | May 1946 | Mauna Loa caldera | Jan. 1949 |
| None recorded | | Mauna Loa flank | June 1950 |
| None recorded | | Kilauea caldera | June 1952 |

of 1935. Neither was the 1952 nor the 1934 eruption of Kilauea predicted from the seismic prelude. However, re-examination of the records shows that deep earthquakes were recorded before these outbreaks. Prior to the early thirties, the seismograph net was inadequate to locate the earthquake centres with accuracy useful in possible prediction of eruption. The dates of deep earthquakes measured

during the last twenty years, and the dates of volcanic eruption during the same time, are tabulated below. Future study may indicate whether the apparent correlation is real or merely coincidence.

## VI. Declining Phase of Primitive Shield-building Activity

Decline in vigour of the primitive shield-building activity has been deduced from field mapping on Hualalai, Mauna Kea, and other shield volcanoes of the Hawaiian group. Macdonald (1949b, p. 1556–65) describes lavas that suggest decline in vigour of primitive shield-building activity at the following major volcanic centres: Kauai, Waianae, East Molokai, Lanai, Kahoolawe, Haleakala, Mauna Kea, and Hualalai. From unpublished field observations, I would add to the list: Koolau, West Maui, and Kohala. Because only the uppermost part of the shields are exposed in many places, and because of the chemistry of the rocks, I would also add the Leeward Islands. If this enlarged list is correct, only three Hawaiian shields, West Molokai, Mauna Loa, and Kilauea, do not exhibit the declining stage of shield-building activity. In the upper part of many of the shields, superimposed lava-flows are separated by a local erosional unconformity or a layer of soil on the lower flow, indicating that eruptions were separated by greater time-intervals than prevailed between eruptions during the vigorous primary stage. Also in the upper part, pyroclastic cones at the vents are more common, with an associated apron of vitric ash that thins away from the vent.

Differences in lava type are associated with the change in geology in the upper part of the shields. Thus the lavas commonly contain abundant phenocrysts of plagioclase; monoclinic pyroxene is found as phenocrysts in some of the lavas and is commonly associated with olivine phenocrysts; some lavas contain an abundance of both augite and olivine, called picrite of the ankaramite type (Macdonald, 1949b, p. 1548). No augite phenocrysts are found in most of the lavas of the primitive shield-building stage. This absence of phenocrystic augite is so consistently true among the lavas of those shields whose structure and geology are best known that one is inclined to suspect that any Hawaiian lava that contains augite as phenocrysts should be assigned to a declining stage of activity. Besides the difference in content of phenocrysts, these lavas commonly contain andesine plagioclase and interstitial alkali feldspar in the groundmass.

Low silica xenoliths are abundant in the lavas of the declining stage, and are sometimes found as coated bombs among the pyroclastic deposits near the vents. Xenoliths in the cores of coated bombs are angular to sub-angular fragments which appear to have been broken from material rigid enough to fracture. The xenoliths have a wide range of mineral composition and are plutonic in appearance. The most abundant are dunite, a few are anorthosite, a few are pyroxenite, and many contain combinations of the three principal minerals in different proportions. The olivine, pyroxene, and calcic plagioclase in the xenoliths have optical properties and presumably compositions, similar to the phenocrysts of these lavas.

Analyzed specimens of lavas from Hualalai and Mauna Kea, considered from their field relations to represent the declining primitive activity of these volcanoes, are all lower in silica than primitive-stage lavas of comparable magnesia content (Fig. 4). No analyses are available from rocks of the primitive stage of these two

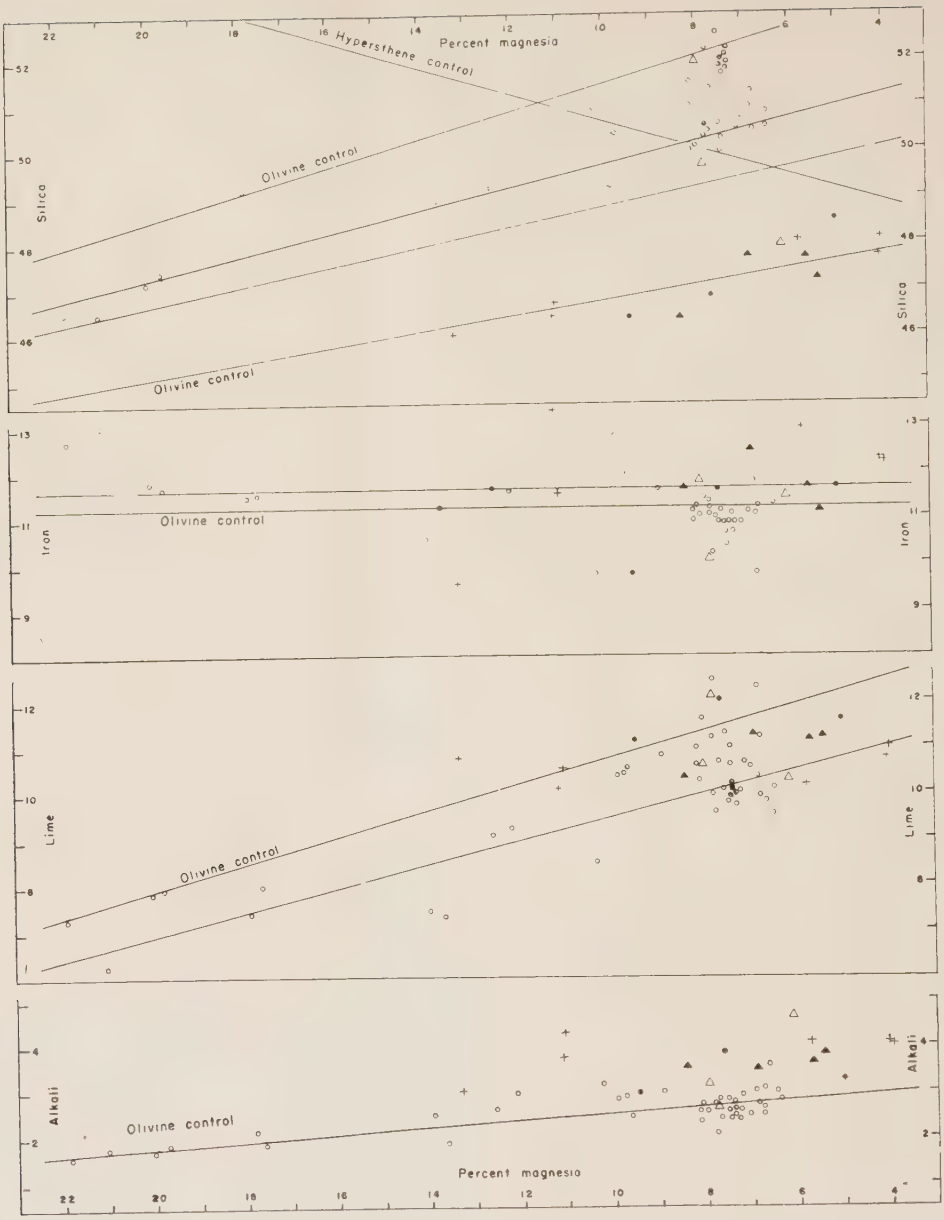


Fig. 4. Diagram comparing analyses known to represent the declining stage of activity of several volcanoes of Hawaii with the data from Fig. 2 and 3 (plotted as open circles). Open triangles, Kohala both primitive and declining stage; solid triangles, Mauna Kea; cross, Hualalai; solid circles, Niihau.

volcanoes. However, two analyzed specimens from the primitive shield of Kohala volcano plot with the higher silica rocks of the primitive stage, and one Kohala specimen from the upper part of its shield plots with the low silica rocks of the declining stage from Hualalai and Mauna Kea. Of the fourteen analyses so plotted, eleven show nepheline as well as olivine in the norm, and only three show quartz in the norm. All analyses of the suite from declining-stage lavas differ from all analyses of the suite from primitive-stage lavas in two respects: they are *under*-saturated with respect to silica, and are richer in alkali with respect to magnesia. The difference in chemistry between a given decadent suite and a given primitive suite, for instance between the Kohala rocks, cannot be expressed in quantities of phenocryst olivine, hypersthene, augite and plagioclase, either added to or subtracted from either suite; part of the difference is always an excess or lack of silica.

No satisfactory explanation has yet been proposed for this desilication based on fractional crystallization alone. Removal of hypersthene crystals can perpetuate an original state of undersaturation, but will not produce desilication of residual melt. The ratio of alkalies and of silica to magnesia in the decadent-stage lavas does not fit with the concept that the decadent magmas were initially undersaturated in silica because they contained more dissolved olivine. The only explanation for the compositions of these rocks that offers much promise seems to call for fractional crystallization superimposed on actual removal of free silica, or addition of soda and lime, or a combination of both.

## VII. Origin of Primary Hawaiian Magma

### 1. *Summary of facts to be taken into consideration*

The following is a summary list of characteristics that must be explained by, or be compatible with, a satisfactory theory of the origin of Hawaiian magma. In the preceding pages, a distinction has been made between those characteristics of Hawaiian eruption and its products that are precisely defined by evidence, those that are suggested by substantial deduction, and those that are mere guesses. Those distinctions are not repeated here.

1. Every Hawaiian volcano has had a stage of vigorous activity and has then begun to "die" with a consistent pattern of events.

2. The "dying" has in general proceeded from west to east along the Hawaiian chain.

3. Hawaiian primitive magma has been made available in batches, the compositions of which differ slightly in the proportion of plagioclase to pyroxene components and more significantly in the small amounts of excess silica.

4. Differences in chemical composition between batches cannot be expressed in quantities of phenocrystic minerals, but can be expressed in quantities of free silica.

5. During the vigorous shield-building stage, each batch of magma is formed and maintained under temperature-pressure conditions that prevent any change of its composition by fractional crystallization and removal of olivine phenocrysts

while it is being exhausted by frequent eruption to the surface. Products of these eruptions do not contain xenoliths of dunite. During its rise to the surface, some of the magma may be purged of or enriched in olivine phenocrysts, thus erratically producing relatively small amounts of basalt and picrite.

6. During the declining phase, bodies of magma remain for sufficient periods of time under temperature-pressure conditions which permit gravitative settling of phenocrysts of olivine, augite, and plagioclase, to produce upon final eruption porphyritic lavas of different compositions. Many of these lavas contain xenoliths of dunite, and other combinations of the phenocrystic minerals. Either at the time of melting or during the period of fractional crystallization, these magmas became notably undersaturated in silica and enriched in alkalies with respect to magnesia.

7. Lava in primitive shield-building eruptions rises rapidly from its source to the surface, and eruptions are repeated frequently. This mobility is credited to high initial content of volatile material.

8. Decadent-stage eruptions are infrequent; perhaps the lava rises sluggishly from its source to the surface. These lavas exhibit high volatile content when they reach surface.

2. *Composition of the earth's crust from which magma is formed*

The first limitation placed on reasoning about the nature of the local crust is imposed by the general chemical composition of Hawaiian magma. The great volume of primitive magma required in Hawaiian volcanic history contains no normative olivine, but essentially is a melt of pyroxene and plagioclase. This melt can be produced either by complete melting of a crust rock that had practically the same composition, i.e., a silica-saturated basalt, or by partial melting of a crust rock that contains excess olivine, a peridotite. If the first assumption is accepted, the effective melting temperatures attained in the process of producing the magma are not limited by the composition of the melt. If the second assumption is accepted, the composition of the ultimate melt dictates that the effective melting temperatures attained must not exceed the liquidus of basalt plus olivine that is present in equilibrium in the crustal rock at the prevailing pressure.

Two more limitations are imposed by the fact that each Hawaiian volcano dies with a consistent pattern of changes that implies exhaustion of the urge to erupt as well as exhaustion of the supply of eruptable material. Considering only the exhaustion of material, if the assumption is accepted that the crust was composed of basalt of the correct composition, it must be stipulated that the amount of such basaltic crust was limited, or that the heat supply was exhausted. If a crust of peridotite is assumed, a limitation on the amount of melt of basaltic composition, available in a limited space, is contained in the assumption, but a limit on the amount of heat applied must be provided in the mechanism called upon to cause the melting, inasmuch as excessive olivine must not be dissolved. The exhaustion of the urge to erupt, which is possibly a depletion of original volatile content with consequent increase of specific gravity, poses a separate problem, whether the material is melted basalt or peridotite, or is a relict substratum of basaltic glass.

A fourth limitation is introduced by interpretation of the few existing data on the physical properties of the crust in part of the Pacific Basin. Recent seismic refraction measurements (Raitt, quoted in Ewing and Press, 1952) suggest a thin layer of sediments on a basement layer about 5 km thick with a compressional wave-velocity about 6·8 km/sec, lying on rock having a compressional wave-velocity of 8·1 km/sec. In terms of familiar rock, the 5-km layer might be basalt, and the deeper rock possibly dunite.

It seems improbable that basaltic magma is now forming so near the surface as to be within Raitt's upper 5-km layer. Neither is it probable that quantities of basaltic liquid could be extracted from rock with a compressional wave-velocity of 8·1 km/sec. Could it be that the picture of crustal composition deduced from the refraction studies represents a layering derived from a crust that earlier was peridotite, the 8·1 material representing residual unmelted olivine, and the 6·8 material representing the pyroxene-plagioclase component of peridotite that was melted and squeezed out? Could it be that in the vicinity of the active volcanoes of Hawaii, the postulated peridotite is still present and is now furnishing melted pyroxene and plagioclase as primitive basaltic magma?

The concept of a globe-encircling voluminous substratum of basaltic glass that could be melted and erupted has been abandoned by its most ardent champion (Daly, 1944, p. 1380) because of unfavourable geophysical evidence. If its dimensions be reduced to the point where it could be permitted by the geophysical data, it loses all its unique characteristics that appealed to geologists and might as well be thought of as small bodies of locally melted crystalline crust.

In this discussion, it is assumed that the Hawaiian magma is melted from a crust of peridotitic crystalline rock. It will also be accepted as a limitation that the amount of heat for melting must not be such as to cause the early generated magma to exceed a definite temperature.

### 3. *Melting processes*

Liquefaction of part of the crystalline peridotite may be accomplished either by adding heat sufficient to melt, by releasing pressure and lowering melting point below existing temperature, or by a combination of both. Crustal temperature at a given point may be increased by three processes, or combinations thereof, that are currently more or less acceptable: adding heat by exothermic nuclear processes within the constituents of the crust at that point; adding heat by convection from deeper, hotter regions in the mantle; or adding heat from friction produced by dynamic processes.

Some of the specifications set forth appear to demand a resurgent process to explain the melting of separate batches, and to demand an upper limit to the amount of heating just short of that required to dissolve olivine in appreciable quantity. Heating by exothermic nuclear reactions, in itself, seems to be not a resurgent process; heating by convection is not resurgent in the time-spans required, nor does it contain within the process a limit to the amount of heat that can be added. The process of adding heat by friction can meet both requirements if the dynamic disturbance that creates the friction is applied resurgently, and if it reaches about the same intensity in each maximum application. Such a dynamic process seems to be available.

Directed stresses are being applied constantly to the earth's crust by tidal forces and by forces incident to the behaviour of the earth's axis of rotation. The resultant of these stresses has a grand maximum which occurs at times when there is coincidence of all the maxima of the different cyclical stresses, each of which has a different period. The resultant of these stresses should have a distortional effect on the equatorial bulge, because some of the component stresses change their sense cyclically with respect to the equatorial plane of the earth.

H. O. Wood (1917) discussed the resulting strains, and suggested the possibility that some cyclic response to their changes in intensity might be found in the behaviour of volcanoes. He pointed out that a maximum of strains due to free and forced nutation would have a period of about 130 years.

In a study of the thirteen-year record of ground tilt at one station on the rim of Kilauea covering the years 1912 to 1925 (Jaggar and Finch, 1929, p. 51), it was suggested that part of the observed tilting phenomena might be explained if ". . . a winter solstice tidal effect acts on the east-west fissure of the Hawaiian ridge, owing to a solar pull southward on the great mass of the ridge and on the equatorial protuberance . . . ."

Further study of the ground tilt at the same station at Kilauea between 1925 and 1946, during a period of relative inactivity of the volcano, showed an annual loop of tilt, apparently unexplained by the influence of temperature or of known volcanic activity, which reversed its sense in October and April (Powers, 1947). It was suggested that this tilt might be related in some way to the change in direction, at equinox, of the horizontal component of the sun's tidal pull on the earth.

If the resultant of these cyclical stresses, i.e., tidal pulls from members of the solar system and distortion from the Chandlerian free nutation, by a kneading action on the equatorial bulge of the crust, is competent at its maximum to melt plagioclase and pyroxene from the peridotite of the crust at a critical depth, it is a process for the production of magma which is cyclically recurrent and contains its own limit on the amount of heat introduced.

4. *Evidence of cycles in Hawaiian activity*

If cyclic forces are to be credited with the formation of Hawaiian magma, cyclic influence should be demonstrable from the record of Hawaiian volcanic activity. Unfortunately, the record is neither long enough nor complete enough to provide a satisfying demonstration either for or against the presence of cycles.

Several measurable phenomena of Hawaiian activity would be expected to show cycles of recurrence. Probably the timing of the deeper local earthquakes should be most closely associated with the postulated kneading of the equatorial bulge. The determination of even an approximate depth of focus of Hawaiian earthquakes has been possible only since about 1930, and the record since that date is by no means complete. Instrumentation is being constantly improved at the Hawaiian Volcano Observatory, and eventually the record of deeper earthquakes will yield significant information. At present the record shows in general

that frequency of deeper earthquakes has been about three times greater during September and about twice greater throughout the periods July–October and January–April than during the periods June–July and November–December (Fig. 5). The data are too few to form the basis for a worthwhile conclusion.

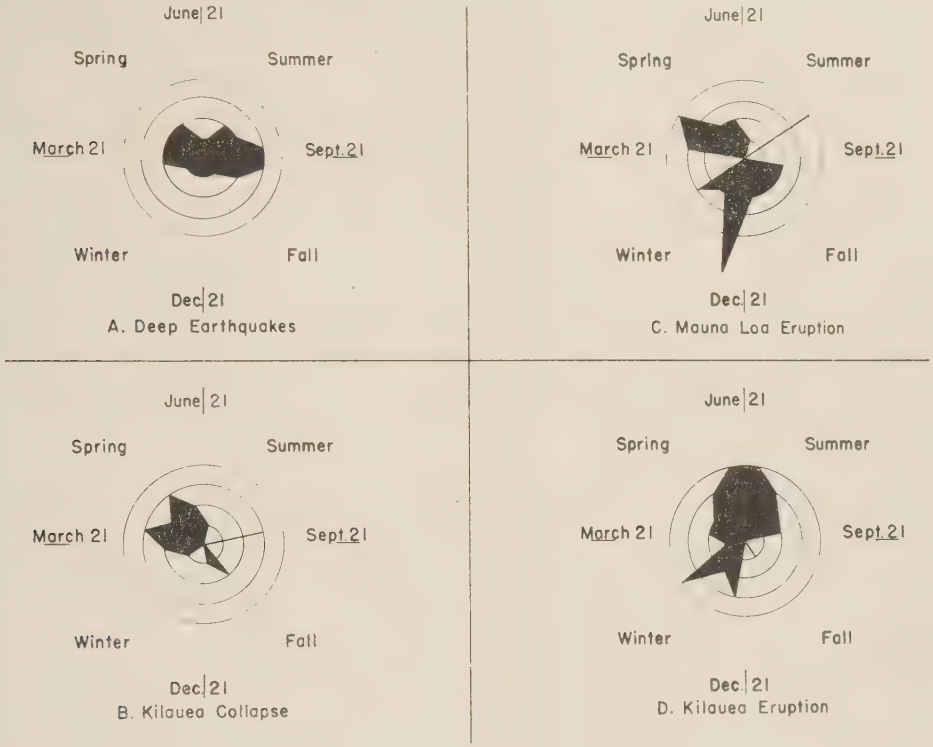


Fig. 5. Asymmetric distribution throughout the solar year of four types of volcanic event: A—deep (ca 50 km) Hawaiian earthquakes; B—collapse at Kilauea associated with sudden withdrawal of magma from surface-lava lake; C—outbreak of historic eruptions of Mauna Loa; D—outbreak of historic eruptions of Kilauea.

Closely associated with earthquake occurrence is the spectacular phenomenon of sudden subsidence of Kilauea's liquid-lava lake that must be caused by subsurface escape of lava through cracks in the lava conduit and resultant draining of the liquid in the conduit above the point of rifting. Such flank eruptions were observed in 1823 and 1840; the others must have been submarine eruptions. Twenty of these sudden drainings of the lava lake have been recorded; twelve took place during March through June, and three took place between August 30 and September 21, in both instances more than double the average number expectable in both periods. This statistical family is obviously too small to show more than a suggestion that the distribution of episodes of withdrawal is not entirely random.

Recorded dates of eruption are convenient data to tabulate in an appraisal of the validity of cyclic behaviour. However, the record of eruptions prior to 1930 does not include episodes of subterranean activity that can be detected only

instrumentally, but which are equally as important as observed surface eruptions in a study for the purpose. Several of these instrumentally observed activities have taken place in recent years, and may well have been equally frequent in the years before they could be detected. Another objection to the use of dates of eruption to determine cyclic influence is that actually the cyclic or non-cyclic recurrence of the stimulation to eruption is the significant fact, not the timing of surface eruption. The time-lag between the event that stimulated eruption and the actual eruption at the surface cannot be assumed to be constant.

Mauna Loa has had thirty-four recorded and dated outbreaks, and Kilauea has had thirty-three recorded starts of eruption, including both the beginning of important rift flows and crateral overflows as well as the return of lava to an inactive crater after a period of dormancy. The distribution through the year is graphed in Fig. 5.

The distribution through the year of these observed eruptions suggests some controlling factor other than pure chance, but the statistical family is too small, regardless of the incompleteness of the data, to justify more than that comment. Mauna Loa erupted significantly more than the average number of times for the period between December 22 and January 13; Kilauea shows more than average preference for the period June 22 to July 14, and a slight preference for the period December 22 to February 27.

Stearns and Macdonald were convinced that a study of the statistics gave no support to any theory of cyclic behaviour of Hawaiian volcanoes (1946, p. 88–92, 94–96, 123–128). On the other hand Jaggar, Finch, and others have been equally convinced that behaviour of the volcanoes is cyclic but that the patterns are not yet clearly understood. In this paper it is accepted that the existing inadequate data give no satisfying demonstration, but that they may suggest cyclic behaviour.

## VIII. Proposed Hypothesis of Origin and Behaviour of Hawaiian Magma

Forced and free nutational forces constantly distort the equatorial bulge of the earth's crust. The intensity of each of these forces varies cyclically. At times of coincidence of the maxima of all such forces, it is suggested that the distortion of the bulge adds enough heat to the normal thermal gradient to melt plagioclase and pyroxene in a zone of rather narrow vertical dimension in a crystalline peridotite crust. The annual kneading maintains heat sufficient to prevent recrystallization of the melt during the time between maxima, and facilitates squeezing the liquid out from the mesh of crystalline olivine into a body of eruptable liquid of silica-saturated basaltic composition.

A major fracture in the crust (opening progressively from west to east), taps this magma and permits continuous or rapidly recurrent eruption until the liquid adjacent to the newly opened fracture is exhausted. At the next recurrence of maximum distortion of the equatorial bulge, more liquid is formed at the same depth in the locality, which in turn is exhausted by eruption. The initial batch and a number of subsequent batches are voluminous and relatively rich in volatile constituents. Their eruption constitutes the primitive shield-building stage of Hawaiian volcanism. As the process is repeated, succeeding melts contain less

volatile material and are less voluminous, and eventually, at each locality, all plagioclase and pyroxene are removed from the narrow-depth zone where melting is possible, leaving a zone of relict dunite, and the production of magma ceases at this locality.

The early volatile-rich batches of magma erupt rapidly. Phenocrysts of olivine, sometimes hypersthene, and sometimes plagioclase form during the rise of the magma to the surface, and enough gravitative movement of olivine crystals takes place erratically during eruption to produce some picrite and some olivine-free basalt.

The later volatile-poor batches of magma with relatively higher specific gravity and viscosity, may be unable to reach the surface in one eruptive effort and may stop at some intermediate depth in the crust. Here, some cooling and crystal fractionation may take place, and the relatively dry magma may take up some water from the adjacent saturated suboceanic crust. Probably some selective assimilation of wall-rock takes place which would contribute slightly to the differentiation that is proceeding by fractional crystallization. Eruption to the surface may eventually take place, and this activity constitutes the decadent stage of Hawaiian volcanic activity. These lava types show differentiation, have abundant phenocrysts, contain xenoliths of the same nature as the early phenocrysts, and the time interval between eruptions is long, in contrast to the characteristics of the primitive shield-building lavas.

Crustal adjustments become necessary after prolonged eruption. If some adjustments are violent, enough heat may be added to that from the cyclic stresses to melt some excess olivine and form the rare ultrabasic liquid required to produce the nephelite-melilite basalts at a few of the volcanoes.

Parts of this hypothesis are subject to rigorous test. More chemical analyses of suites of specimens chosen for the purpose should prove or disprove the concept of batches of magma with originally different silica content. A long and complete record of deep earthquakes and other volcanic events in Hawaii eventually should prove or disprove the presence of cyclic control. More geophysical observations may give definite knowledge of the depth at which Hawaiian magma is formed, and of the probable composition of the local crustal material at that depth.

The proposed process of volcanism, if valid, should be applicable in part only to volcanoes situated along the equatorial bulge. However, its operation probably would be completely obscured by the processes of volcanism associated with great structural deformation in regions where the equatorial bulge is coincident with zones of Cenozoic mountain-building. Also, different lava types would be expected where the bulge crosses the great blocks of sial. Thus, reasonable similarity to the Hawaiian volcanoes, both as to eruptive history and lava type, would be expected among the equatorial-tropical belt volcanoes of the sima-floored parts of the Pacific, Atlantic, and Indian Ocean basins. Similar frequent eruption, but different lava type, would be expected among the volcanoes of the equatorial-tropical belt on those parts of the continents not associated with zones of mountain-building such as equatorial East Africa. The general similarity between most ocean-basin volcanoes and Hawaii, and the comparable type of activity found at the East African volcanoes, perhaps offers some support to the hypothesis.

## IX. APPENDIX A

Published analyses of Hawaiian lavas used in this discussion

| *MgO* | *Silica satur.*[1] | *Rock name* | *Field assgment.* | *Volcano* | *Reference* | *Page No.* | *Analysis No.* |
|---|---|---|---|---|---|---|---|
| *Rocks generally saturated in silica:* | | | | | | | |
| 13·86 | −2·76 | Olivine basalt | primitive | Koolau | WENTWORTH and WINCHELL, 1947 | 71 | 9 |
| 12·41 | −2·10 | ,, | ,, | Kilauea | MACDONALD, 1949a | 74 | 4 |
| 12·04 | −1·68 | ,, | ,, | ,, | ,, | 74 | 5 |
| 10·68 | 0·42 | ,, | ,, | Mauna Loa | MACDONALD AND EATON (in prep.) | Table 9 | 7 |
| 10·18 | 1·02 | ,, | ,, | Koolau | WENTWORTH and WINCHELL, 1947 | 71 | 4 |
| 9·80 | −0·54 | ,, | ,, | Mauna Loa | MACDONALD, 1949a | 63 | 1 |
| 9·68 | −0·06 | ,, | ,, | Kilauea | ,, | 73 | 5 |
| 9·57 | 0·54 | ,, | ,, | ,, | ,, | 73 | 4 |
| 9·14 | 4·56 | ,, | ,, | Mauna Loa | MACDONALD and EATON (in prep.) | Table 9 | 1 |
| 8·83 | −1·44 | ,, | ,, | Kilauea | MACDONALD, 1949a | 74 | 6 |
| 8·09 | 3·78 | basalt | ,, | ,, | ,, | 73 | 8 |
| 8·02 | 2·82 | ,, | ,, | Mauna Loa | ,, | 63 | 9 |
| 8·01 | 2·16 | olivine basalt | ,, | Kilauea | ,, | 74 | 7 |
| 7·98 | 4·26 | basalt | ,, | Kohala | ,, | 87 | 10 |
| 7·96 | 0·96 | olivine basalt | ,, | Kilauea | ,, | 74 | 9 |
| 7·89 | 0·18 | ,, | ,, | ,, | MACDONALD and EATON (in prep.) | Table 9 | 5 |
| 7·80 | 0·72 | ,, | ,, | Kohala | MACDONALD, 1949a | 87 | 9 |
| 7·75 | 0·42 | ,, | ,, | Kilauea | ,, | 74 | 11 |
| 7·69 | 7·74 | basalt | ,, | Mauna Loa | ,, | 63 | 12 |
| 7·68 | 4·08 | olivine basalt | ,, | Mauna Loa | MACDONALD, 1949a | 63 | 5 |
| 7·64 | 2·10 | ,, | ,, | Koolau | WENTWORTH and WINCHELL, 1947 | 71 | 6 |
| 7·62 | 4·26 | ,, | ,, | Kilauea | MACDONALD, 1949a | 73 | 9 |
| 7·61 | 1·26 | ,, | ,, | ,, | MACDONALD and EATON (in prep.) | Table 9 | 4 |
| 7·44 | 4·80 | olivine basalt | ,, | Kilauea | MACDONALD, 1949a | 74 | 13 |
| 7·43 | 7·98 | basalt | ,, | Mauna Loa | ,, | 63 | 14 |
| 7·39 | 2·04 | olivine basalt | ,, | Kilauea | ,, | 74 | 10 |
| 7·37 | 9·96 | basalt | ,, | Mauna Loa | ,, | 63 | 11 |
| 7·36 | 5·28 | ,, | ,, | ,, | MACDONALD, 1949b | 1572 | 4 |
| 7·33 | 5·16 | ,, | ,, | Kilauea | MACDONALD, 1949a | 73 | 10 |
| 7·31 | 8·40 | ,, | ,, | Mauna Loa | ,, 1949b | 1572 | 5 |
| 7·26 | 6·90 | olivine basalt | ,, | ,, | ,, 1949a | 63 | 6 |
| 7·24 | 4·68 | basalt | ,, | ,, | ,, | 63 | 10 |
| 7·21 | 6·24 | ,, | ,, | Koolau | WENTWORTH and WINCHEL, 1947 | 71 | 2 |
| 7·15 | 6·42 | olivine basalt | ,, | Mauna Loa | MACDONALD, 1949a | 63 | 13 |
| 7·14 | 4·32 | basalt | ,, | ,, | MACDONALD and EATON (in prep.) | Table 9 | 3 |
| 7·10 | 8·28 | ,, | ,, | ,, | MACDONALD, 1949a | 63 | 2 |

Appendix A (*continued*)

| *MgO* | *Silica satur.*[1] | *Rock name* | *Field assgment.* | *Volcano* | *Reference* | *Page No.* | *Analysis No.* |
|---|---|---|---|---|---|---|---|
| *Rocks generally saturated in silica:* | | | | | | | |
| 7·04 | 3·90 | basalt | primitive | Mauna Loa | Macdonald and Eaton (in prep.) | Table 9 | 2 |
| 7·03 | 1·26 | olivine basalt | ,, | Kilauea | ,, | 9 | 6 |
| 7·01 | 4·62 | basalt | ,, | ,, | Macdonald, 1949a | 73 | 7 |
| 6·88 | 2·88 | ,, | ,, | Koolau | Wentworth and Winchell, 1947 | 71 | 5 |
| 6·76 | 2·70 | basalt | ,, | Kilauea | Macdonald, 1949a | 74 | 15 |
| 6·73 | 4·02 | ,, | ,, | ,, | ,, | 73 | 6 |
| 6·72 | 2·16 | ,, | ,, | Koolau | Wentworth and Winchell, 1947 | 71 | 1 |
| 6·70 | 4·74 | ,, | ,, | ,, | ,, | | 7 |
| 6·38 | 3·48 | ,, | ,, | Kilauea | Macdonald, 1949b | 1572 | 2 |
| 5·90 | 5·10 | ,, | ,, | Mauna Loa | Macdonald, 1949a | 63 | 4 |
| *Rocks generally under-saturated in silica:* | | | | | | | |
| 13·25 | −12·00 | olivine basalt | declining | Hualalai | Macdonald, 1949a | 78 | 1 |
| 12·60 | −15·36 | ,, | decadent[2] | Niihau | ,, 1947 | 50 | 1 |
| 12·42 | −10·08 | ,, | ,, | ,, | | | 2 |
| 11·08 | −8·82 | ,, | declining | Hualalai | ,, 1949a | 78 | 2 |
| 11·07 | −14·62 | ,, | ,, | ,, | ,, | | 3 |
| 9·93 | −10·02 | ,, | decadent[2] | Niihau | ,, 1947 | 50 | 4 |
| 8·40 | −4·56 | ,, | declining | Mauna Kea | ,, 1949a | 83 | 1 |
| 7·85 | −14·16 | ,, | decadent[2] | Haleakala | ,, 1942 | 309 | 5 |
| 6·89 | −3·66 | ,, | declining | Mauna Kea | Macdonald, 1949a | 83 | 6 |
| 6·37 | −6·84 | ,, | decadent[2] | Halcakala | ,, 1942 | 309 | 4 |
| 5·77 | −0·60 | basalt | declining | Hualalai | ,, | 78 | 5 |
| 5·68 | −1·56 | ,, | ,, | Mauna Kea | ,, | 83 | 5 |
| 5·43 | −4·26 | olivine basalt | ,, | ,, | ,, | 83 | 4 |
| 4·02 | −0·84 | basalt | declining | Hualalai | ,, 1949a | 78 | 4 |
| 3·97 | 2·58 | gabbro | ,, | ,, | Macdonald, 1949a | 78 | 6 |

[1] In terms of excess or deficiency of silica after computing normative feldspar, pyroxene, apatite, and iron ores.

[2] Known from field relations to belong to post-erosion senescent stage of activity.

## Appendix B

It is possible to express the differences in silica and magnesia content of several analyzed lavas from Koolau volcano in terms of phenocrystic olivine and hypersthene. This particular suite is chosen because phenocrysts of both minerals are present in some of the rocks. However, the computation is not sufficient in itself to demonstrate that the rocks were formed by appropriate addition or removal of combinations of these crystals; the process must be visualized in an assumed magma chamber, and the theoretical products must resemble the rocks described.

A first solution is offered using the silica-magnesia content of Macdonald's

average of fifty-three Hawaiian olivine basalts, point "M" on Fig. 6, as the source magma.

| | | |
|---|---|---|
| 1. M plus 1·6% ol plus 18·0% hyp | yields composition | 9948 |
| 2. M minus 12·5% ol | yields composition | M2 |
| 3. M2 plus 9·0% hyp | yields composition | 9991 |
| 4. M2 plus 22·6% hyp | yields composition | 9980 |
| 5. M2 minus 1·8% ol plus 15·2% hyp | yields composition | 9986 |
| 6. M2 minus 6·7% ol plus 18·1% hyp | yields composition | 10404 |
| 7. M2 minus 7·6% ol plus 23% hyp | yields composition | 10403 |

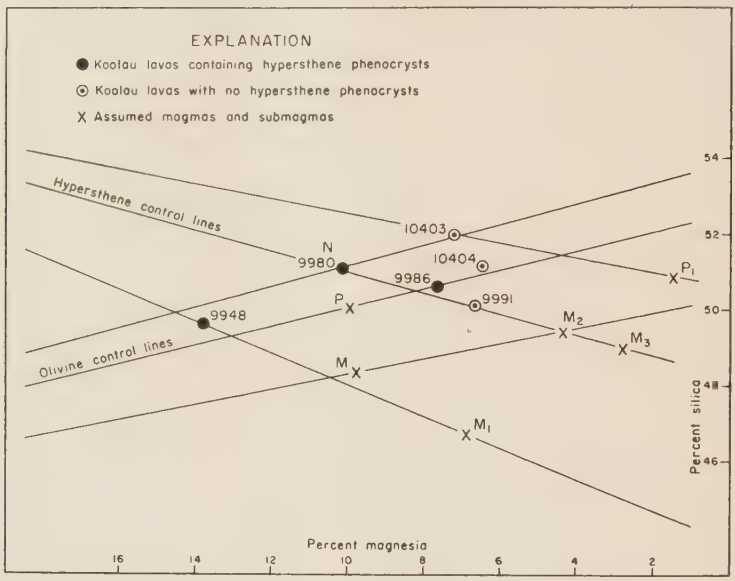


Fig. 6. Graph upon which differences in silica and magnesia content of some Koolau rocks are computed as olivine and hypersthene. Numbers refer to rock specimens described by Wentworth and Winchell, 1947. Hypersthene and olivine control lines determined from Fig. 2.

Several limiting conditions become apparent under which these movements of crystals could have taken place.

1. All submagmas must have formed in a zone below the top of the assumed magma chamber, because each submagma requires the addition of hypersthene crystals by gravity settling (each step except No. 2).

2. The temperature in the zone of submagma formation must have fluctuated above and below the crystallization point of olivine but remained above that of hypersthene, inasmuch as partly resorbed olivine crystals (without reaction rims) are present in the lavas, though most of the increment hypersthene crystals must have been resorbed prior to eruption, i.e.,

specs. 9991 and 10404 contain a few partly resorbed olivines and no hypersthene phenocrysts (though the norm contains 18 per cent and 14 per cent hypersthene, respectively),

specs. 10403 contains a few partly resorbed olivines, and a few microphenocrysts of hypersthene enclosed in a shell of pigeonite (norm contains 20 per cent hypersthene),

specs. 9948, 9980, and 9986 contain phenocrysts both of partly resorbed olivine and of hypersthene, but groundmass pyroxene is pigeonitic.

3. The ultimate composition of the residual liquid in the upper zone of the magma chamber would have to range through the area on the graph that includes M1 and M3, depending on the rate of temperature-drop one prefers; a rapid cooling through the crystallization point of olivine would permit subtraction of a minimum of olivine from the liquid, and vice versa.

4. The volume of the upper liquid that yielded migrating hypersthene phenocrysts must exceed the volume of the submagma liquids, because the required bulk of hypersthene crystals (up to 23 per cent in step 7) could not precipitate from an equal volume of liquid before it would yield augite rather than hypersthene. This postulated large volume of liquid in the top of the magma chamber, depleted in the enstatite molecule, is not represented in any known rock in the Koolau primitive shield. Hundreds of these rocks have been examined with the microscope, and all contain pigeonitic pyroxene (if not hypersthene) in the groundmass. It is improbable that a large body of liquid in the top of the presumed magma chamber could have escaped extrusion during the countless eruptions that built the Koolau primitive shield.

A second solution is offered, using an original composition at point "N," equivalent to rock composition 9980:

All rock compositions can be expressed without adding hypersthene, three of the seven by moving olivine alone, and four of the seven by subtracting little or no olivine, but subtracting hypersthene. This would imply that differentiation was accomplished near the top of the magma chamber, and in half the cases the temperature of the magma must have dropped quickly through the crystallization range of olivine, then held steady while hypersthene crystals formed and settled out of the liquid. This cooling pattern seems improbable, and, furthermore, most of the rocks erupted contain olivine crystals.

A third sample solution starts from an original magma with silica and magnesia at point "P."

| | |
|---|---|
| 1. P minus 6·0% ol | yields composition 9986 |
| 2. P minus 4·5% ol minus 6·5% hyp | yields composition 9991 |
| 3. P minus 9·8% ol plus 2·5% hyp | yields composition 10404 |
| 4. P minus 4·5% ol plus 9·2% hyp | yields composition 9980 |
| 5. P minus 12·7% ol plus 10·6% hyp | yields composition 10403 |
| 6. P plus 7·9% ol plus 5·5% hyp | yields composition 9948 |

Special conditions stipulated:

1. Most of these submagmas must have been produced near the upper part of the magma chamber. All but one has been depleted in olivine crystals, and over half have been appreciably enriched in hypersthene crystals.

2. The temperature of most submagmas must have been lower than the

crystallization point of olivine, but ranged above and below that of hypersthene. Rock 10403 contains relict olivine, but all the increment hypersthene must have melted; in rocks 9980 and 9948 only part of the increment hypersthene was melted prior to eruption. The submagma that produced rock 9991 (a common lava type) must have precipitated both olivine and hypersthene to reach the required composition, then must have been reheated above the melting point of hypersthene before eruption. These fluctuations of temperature required seem improbable as a natural pattern of behaviour.

3. Some residual liquid, depleted in the enstatite molecule (composition in the direction of P1) was produced but not erupted.

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## Book review

**Chemical Analyses of Spanish Rocks.** By J. M. Fúster, E. Ibarrola, and M. P. Lobato (*Analisis quimicos de rocas españolas*)

Con un pròlogo por D. Maximino San Miguel de la Càmara. Monografias del Instituto "Lucas Mallada" de Investigaciones Geologicas Num. 14. Consejo Superior de Investigaciones Cientificas. Madrid, 1954. xxiii + 139 pages.

The book is essentially a list of chemical analyses expressed in weight percentages of the twelve major oxides of igneous and metamorphic rocks of Spain and her African territories. As shown by the bibliography (ninety-five numbers), original papers with analyses of Spanish rocks are scattered throughout a great many periodicals of many lands. All these have been brought together in the present volume. It is interesting to note that the first analyses of Spanish rocks were published by Collins in 1885 (Rio Tinto province). But rocks from the Canary Islands were analyzed as early as 1848 (by Saint-Claire Deville).

From Spain proper 206 different analyses now exist; in addition, the Canary Islands, Spanish Morocco, and the Spanish Territories of the Gulf of Guinea contribute with 250 analyses, making a grand total of 456 analyses.

Short notes explicatory to the tables are printed in four languages: Spanish, French, English, and German.

Tom F. W. Barth

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## Announcement

### The Geophysical Laboratory—Johns Hopkins University Predoctoral Fellowships in Petrology and Geochemistry

The Geophysical Laboratory of the Carnegie Institution of Washington and the Geology Department of The Johns Hopkins University, Baltimore, Maryland, are co-operating in the award of two two-year predoctoral fellowships in petrology and geochemistry. Applicants for the awards must have completed a year of graduate work in the geologic sciences, and be proficient in physical chemistry.

During the first year the fellows spend most of their time at the University completing courses and other requirements for the doctorate. The second year is devoted to research at the Geophysical Laboratory leading toward a dissertation. Stipend is $2,400 the first year and $2,800 the second year.

Application for a fellowship, supported by transcripts and recommendations, should be sent to Professor Ernst Cloos, Chairman, Geology Department, The Johns Hopkins University, Baltimore 18, Maryland. Application for a fellowship starting with the academic year in October must be filed by March 1. Awards are announced on April 1.

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## ERRATUM

In the paper by Julian R. Goldsmith and Fritz Laves on "potassium feldspars structurally intermediate between microcline and sanidine" which appears on pages 100 to 118 of volume 6 (1954), Figs. 2 and 3 on page 102 have unfortunately been transposed.

# INFORMATION FOR CONTRIBUTORS

## I. GENERAL

1. Papers on Geochemistry should be submitted to the editors for the appropriate country or language (*Papers on Cosmochemistry should be sent to Prof. F. A. Paneth, F.R.S.*). Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. The preparation of progress reports and review articles will be invited by the Editors from time to time. The Journal will appear as independent and complete numbers, which will be sold separately and combined into volumes of about 300 pages.

2. Only papers which have not been previously published will be accepted. Authors must agree not to publish elsewhere a paper submitted to and accepted by *Geochimica et Cosmochimica Acta*.

3. Fifty reprints of each paper are provided free. Additional copies can be purchased if ordered at the time the first proofs are returned.

## II. MANUSCRIPT REQUIREMENTS

1. Manuscripts must be written in one of the three official languages, English, French, or German.

2. The manuscript should be an original typewritten copy (not a carbon). The text must be ready for printing and should be carefully checked for errors. Authors will receive proofs for correction.

3. Illustrations should accompany the manuscript mounted on separate sheets. Line diagrams that require to be redrawn should include all relevant details. Half-tone illustrations should be restricted to the minimum necessary. Photographs should be enlarged sufficiently to permit their clear reproduction, and if words or numbers appear in them, two copies should be sent, one clearly printed and the other without inscription. All illustrations should be provided with descriptive legends, which should be given on a separate sheet.

4. References in the text should be given by quoting the author's name and year of publication, i.e. AHRENS (1952). **Full references should be listed at the end of each paper, in alphabetical order, in the following manner:**

AHRENS, L. H. (1952) *Geochim. et Cosmochim. Acta*, **2**, 168.

and should include the standard abbreviated title of the journal, year, volume number and page number.

5. The text of articles submitted should be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract in English. Such an abstract may, however, be submitted by the author in the language of the original typescript for translation into English by the editorial staff.

6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

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